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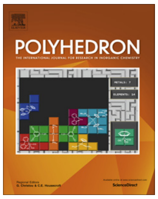

Molecular structures of cobalt complexes of 2-aza-2-[*p*-methylbenzyl]-5,10,15,20-tetraphenyl-21-carbaporphyrin: [Co(2-NCH_2-*p*-$C_6H_4CH_3$-21-*m*-$CH_2C_6H_4CH_3$NCTPP)L] (L = Cl^-, N^*CS^-)

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ABSTRACT

Two experimentally well characterized four-coordinate complexes of the general formula [Co(2-NCH_2-*p*-$C_6H_4CH_3$-21-*m*-$CH_2C_6H_4CH_3$NCTPP)L] (with L = Cl^- and N^*CS^- for **3** and **4**) are considered for this study. The crystal structures of the paramagnetic chloro(2-aza-2-[*p*-methyl benzyl]-5,10,15,20-tetraphenyl-21-*m*-xylyl-21-carbaporphyrinato-N,N′,N″) cobalt(II) octane solvate [Co(2-NCH_2-*p*-$C_6H_4CH_3$-21-*m*-$CH_2C_6H_4CH_3$NCTPP)Cl]·0.5C_8H_{18} (**3**·0.5 C_8H_{18}) and thiocyanato-N-(2-aza-2-[*p*-methylbenzyl]-5,10,15,20-tetraphenyl-21-*m*-xylyl-21-carbaporphyrinato-N,N′,N″) cobalt(II) [Co(2-NCH_2-*p*-$C_6H_4CH_3$-21-*m*-$CH_2C_6H_4CH_3$NCTPP)(NCS)] (**4**) were established. The geometry around the Co^{2+} ion in **3**·0.5 C_8H_{18} (or **4**) is a distorted tetrahedron, with C_{2v} symmetry. The magnitude of the zero-field splitting (ZFS) parameter (D) was reported to change from 44.5 cm^{-1} in **3** to 30.0 cm^{-1} in **4** through DC magnetic susceptibility determinations. The |*D*| value can be related to the magnitude of the ligand-field splitting parameter of the axial k-donating Cl^- ligand of **3** and the axial π-accepting NCS^- ligand of **4** at the cobalt sites.

1. Introduction

An N-confused porphyrin (NCP), first isolated in 1994 independently by Furuta [1] and Latos-Grazynski [2], is a porphyrin isomer with an inverted pyrrole ring. There are three main reaction sites in the confused pyrrole ring, including external nitrogen (2-N), external carbon (3-C) and internal carbon (21-C) atoms [1–4]. At the external nitrogen atom of NCP(2-N), an electrophilic reaction can take place yielding alkylated products [1–4]. Lin et al. [5] reported the synthesis of 2-aza-2-[*p*-methylbenzyl]-5,10,15,20-tetraphenyl-21-carbaporphyrin [2-NCH_2-*p*-C_6H_4-CH_3NCTPPH] (**1**). The free base **1** can provide N_3 or N_3C coordinated sites and these are effectively utilized in generating the nickel complex (2-azo-2-[*p*-methylbenzyl]-5,10,15,20-tetraphenyl-21-carbaporphyrinato-N,N′,N″) nickel (II), [Ni(2-NCH_2-*p*-C_6H_4-CH_3NCTPP)] (**2**), with an N_3C coordination core [5]. Several X-ray structures of four-coordinate cobalt(II) N-confused porphyrin complexes and their zero-field splitting (ZFS) parameters (D) have been reported [6–8], wherein the axial ligand in these cobalt(II) complexes is the Cl^- ion. The magnetic anisotropy is quantified in terms of the ZFS parameter (D), which appears to be sensitive toward ligand substitution [9–12]. Furthermore, Cl^- (with a weaker ligand field splitting parameter) and N^*CS^- (with stronger ligand field splitting parameter) ions were selected as axial ligands in this study [9]. In order to investigate the effect of the ligands for tuning the magnetic anisotropy in Co (II) 2-N substituted N-confused porphyrin complexes, we have extended our studies to the insertion of cobalt ions into **1**, leading to the cobalt(II) complexes chloro(2-aza-2-[*p*-methylbenzyl]-5,10,15,20-tetraphenyl-21-*m*-xylyl-21-carbaporphyrinato-N,N′,N″) cobalt(II) octane solvate, [Co(2-NCH_2-*p*-$C_6H_4CH_3$-21-*m*-$CH_2C_6H_4$-CH_3NCTPP)Cl]·0.5C_8H_{18} (**3**·0.5C_8H_{18}), and thiocyanato-N-(2-aza-2-[*p*-methylbenzyl]-5,10,15,20-tetraphenyl-21-*m*-xylyl-21-carbaporphyrinato-N,N′,N″) cobalt(II), [Co(2-NCH_2-*p*-$C_6H_4CH_3$-21-*m*-$CH_2C_6H_4CH_3$NCTPP)(NCS)] (**4**) (Scheme 1). Complexes **3** and **4** are chosen as the targets for magnetic property measurements. To examine the effect of the Cl^- (**3**) and NCS^- (**4**) ions in the axial positions on the magnetic anisotropy of complexes **3** and **4**, the ZFS parameters (D) of these complexes were estimated using DC magnetic susceptibility measurements. For this study, the diamagnetic compound **2** is used as a diamagnetic subtraction factor for paramagnetic compounds **3** and **4** in the DC magnetic susceptibility determinations. In other systems, Krzystek and coworkers reported

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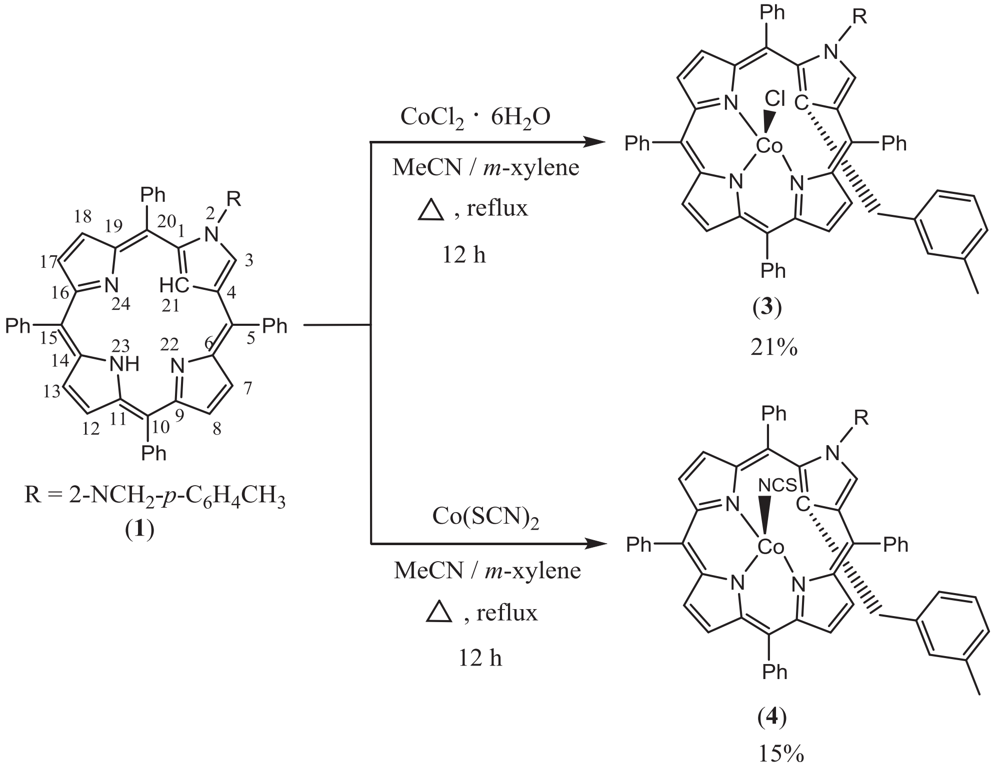

Scheme 1. Synthesis of **3** and **4** (the numbering of **1** on the far left is used for the nomenclature of the compounds, and this numbering scheme is consistent with that reported in the literature).

a high-frequency and high-field EPR investigation of manganese N-confused porphyrins [13].

2. Experimental

2.1. Preparation of 3

A mixture of **1** (0.0360 g, 0.05 mmol) and $CoCl_2{\cdot}6H_2O$ (0.0476 g, 0.2 mmol) in a mix of CH_3CN (5 ml) and *m*-xylene (30 ml) was refluxed for 12 h (Scheme 1) [5]. After concentrating the reaction mixture, the residue was dissolved in CH_2Cl_2 (5 ml) and filtered. The filtrate was then concentrated and the residue was purified over a silica gel column (Si 60, 40–63 μm, 10 g) using EtOAc/CH_2Cl_2 [1:99 (v/v)] as the eluent to yield a brown-yellow solution of **3**. Removal of the solvent gave **3** as a brown-yellow solid (0.0094 g, 0.0103 mmol, 21%), which was redissolved in CH_2Cl_2 and layered with octane [octane/CH_2Cl_2 = 2:1 (v/v)] to afford brown crystals for single-crystal X-ray analysis: M.p. 302 °C, MS (ESI), *m*/*z* (assignment, rel. intensity): 880.3 ($[M{-}Cl]^+$, 100%). *Anal.* Calc. for $C_{60}H_{45}ClCoN_4{\cdot}0.27C_8H_{18}$: C, 78.75; H, 5.31; N, 5.91. Found: C, 78.93; H, 5.49; N, 6.20%. UV–Vis–NIR spectrum, λ (nm) [$\varepsilon \times 10^{-2}$, $M^{-1}\,cm^{-1}$] in CH_2Cl_2: 472 (790), 585 (27), 718 (98), 783 (216), 1086 (1.9), 1282 (1.9).

2.2. Preparation of 4

A mixture of **1** (0.036 g, 0.05 mmol) and $Co(SCN)_2$ (0.035 g, 0.2 mmol) was refluxed in a mix of CH_3CN (5 ml) and *m*-xylene (30 ml) for 12 h (Scheme 1). After concentrating the reaction mixture, the residue was dissolved in CH_2Cl_2 (5 ml) and filtered. The filtrate was then concentrated and the residue was purified over a silica gel column (Si-60, 40–63 μm, 10 g) using CH_2Cl_2 as the eluent to yield a brown–green solution of **4**. Removal of the solvent gave **4** as a brown-green solid (0.0072 g, 0.0077 mmol, 15%), which was redissolved in CH_2Cl_2 and layered with octane [octane/CH_2Cl_2 = 2:1 (v/v)] to afford brown crystals for single-crystal X-ray analysis: M.p. 352 °C, MS (ESI), *m*/*z* (assignment, rel. intensity): 801.2 ($[M{-}NCS{-}C_6H_6{-}H]^+$, 100%), 880.1 ($[M{-}NCS]^+$, 90.22%), 938.1 ($[M{-}H]^+$, 8.72%). *Anal.* Calc. for $C_{61}H_{45}CoN_5S{\cdot}1.90CH_3CN$: C, 76.52; H, 5.02; N, 9.50. Found: C, 76.29; H, 5.02; N, 9.28%. UV–Vis–NIR spectrum, λ(nm) [$\varepsilon \times 10^{-2}$, $M^{-1}\,cm^{-1}$] in CH_2Cl_2: 465 (671), 590 (34), 693 (80), 765 (216), 1060 (1.5), 1237 (1.7).

2.3. Magnetic susceptibility measurements

The solid-state magnetic susceptibility was measured under helium on a Quantum Design MPMS7 SQUID susceptometer from 2 to 300 K at a field of 5 kG. The sample was held in a Kel-F bucket. The bucket had been calibrated independently at the same field and temperature. The raw data for **3** and **4** were corrected for molecular diamagnetism. The diamagnetic contribution of samples of **3** and **4** was measured from an analogous diamagnetic metal complex, that is **2**. Details of the diamagnetic correction that were made can be found in the reference by Drago [14].

2.4. Spectroscopy

Elemental analyses were carried out on an Elementar Vario EL cube analyzer. The mass spectra MS(ESI) were recorded on a Thermo Finnigan TSQ Quantum mass spectrometer with an ESI source. UV–Vis spectra were recorded at 300 K on a Varian Cary 60 Conc UV–Visible spectrophotometer. UV–Vis–NIR spectra were recorded at 300 K on a Shimadzu UV-3600 UV–Vis–NIR spectrophotometer.