Racemic iron(III) and cobalt(III) complexes containing a new pentadentate "helmet" phthalocyaninato ligand

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Electronic supplementary information

Synthesis and spectroscopic characterization of **1**: Iron(II) acetate tetrahydrate (44.2 mg, 0.254 mmol), 1,2-dicyanobenzene (194.6 mg, 1.52 mmol) and 4.0 mL methanol were combined in a glass vial, which was then placed in a PTFE-lined stainless steel autoclave and heated for seven days at 130 ˚C. Upon opening the autoclave, a dark brown solution was observed, along with some dark red crystals, suitable for X-ray crystallography, and apparently amorphous solids. The solution was allowed to evaporate and the residue was dissolved in a minimal amount of dichloromethane. This solution was loaded onto a silica gel flash column. A red-brown band remained strongly adsorbed at the top of the column as organic impurities were eluted with 100 mL of a 50% toluene: 50% dichloromethane mixture, followed by 1.0 L of 100% toluene, then 100 mL of a 50% toluene: 50% dichloromethane mixture, then 200 mL of 100% dichloromethane. A broad red-brown band then quickly desorbed and eluted with 100% methanol and was collected. Slow evaporation of the solvent yielded dark red crystals of **1** (46.0 mg, 0.0558-0.0570 mmol, 22.0-22.5 %) based upon the starting iron reagent. Because **1** is obtained with varying proportions of methanol and water as ligand L, the yield must be reported as a range between 22.0% (assuming X is 100% water, with three molecules of methanol present in the crystal lattice) and 22.5% (assuming L is 100% methanol, with two additional non-coordinated molecules of methanol present in the crystal lattice). The relationship between the identity of L and the number of co-crystallized methanol molecules is inferred from crystallographic results. The identity of this sample was confirmed by comparison of its IR and UV-VIS spectra to those of an authentic sample from a similar reaction that was fully characterized *via* X-ray crystallography. Satisfactory elemental analysis of **1** cannot be obtained due to partial solvent loss from the crystal lattice upon drying. IR $\bar{\nu}_{\mathrm{max}}$/cm^{-1} 3413br, 3057w, 2820w, 1623m, 1557s, 1521s, 1472s, 1444s, 1396s, 1353w, 1321m, 1310m, 1296m, 1207m, 1161m, 1144m, 1123s, 1097m, 1079m, 1027s, 1007m, 993m, 964w, 948m, 923m, 880w, 845w, 803w, 778m, 753m, 730vs, 701m, 684w, 666w, 651w, 637w and 625w. These data match with those obtained from an authentic sample of **1** characterized by X-ray crystallography.

Synthesis and spectroscopic characterization of **2**: Cobalt(II) acetate tetrahydrate (91.5 mg, 0.367 mmol), 1,2-dicyanobenzene (281.8 mg, 2.20 mmol) and 4.0 mL methanol were combined in a PTFE-lined stainless steel autoclave and heated for seven days at 70 ˚C. Upon opening the autoclave, a dark brown solution was observed, along with a suspension of very fine violet-colored needle-shaped crystals, determined by IR spectroscopy (KBr disc) in another experiment to be phthalocyaninato cobalt(II), PcCo. Also present on the bottom of the PTFE cup were orange-red X-ray diffraction-quality crystals of **2**. The contents of the cup were stirred and the liquid portion decanted, along with most of the PcCo. Repeated rinsing of the remaining solid with methanol in the cup and decanting of the methanol removed almost all of the PcCo needles, leaving a sample of **2** (35.0 mg, 0.043 mmol) that showed no contamination by IR spectroscopy, on the basis of comparison of its spectrum to that of an authentic sample that had been fully characterized *via* X-ray crystallography. However, a very minute trace of the PcCo crystals was evident upon visual examination under a microscope. Assuming that these crystals represent an insignificant fraction of the total sample mass, the yield of **2** is calculated to be 11.8%, based upon the starting cobalt reagent. In another experiment, a sample of **2** prepared from cobalt(II) acetate tetrahydrate (91.6 mg, 0.369 mmol) and 1,2-dicyanobenzene (281.8 mg, 2.20 mmol) similarly obtained with trace PcCo was dissolved in minimum dichloromethane and loaded onto a silica gel flash column. An orange-red band remained strongly adsorbed at the top of the column while 700 mL of dichloromethane eluted. The orange band then quickly desorbed and eluted when a 50% methanol: 50% dichloromethane mixture was passed through the column. The entire band was collected and allowed to slowly evaporate, yielding orange crystals of **2** (21.4 mg, 0.0264 mmol, 7.2%) that showed no trace of contamination by IR spectroscopy or visual examination under a microscope. Satisfactory elemental analysis of **2** cannot be obtained due to partial solvent loss from the crystal lattice upon drying. IR $\bar{\nu}_{max}/cm^{-1}$ 3413br, 3055w, 2942w, 2827w, 1968w, 1935w, 1830w,1763w, 1719w, 1615m, 1560s, 1534s, 1472s, 1449s, 1398s, 1323m, 1297m, 1210m, 1179w, 1163w, 1146w, 1123m, 1097m, 1078w, 1051w, 1030m, 1013m, 973w, 955w, 925w, 883w, 850w, 805w, 776m, 754w, 729vs, 696m, 684w, 666w, and 653w. These data match with those obtained from an authentic sample of **2** characterized by X-ray crystallography. While **2** is diamagnetic, its solubility in NMR solvents is insufficient to allow the recording of meaningful ^{13}C NMR spectra. A ^{1}H spectrum in CD_2Cl_2 shows a complex series of resonances ranging from 6.3 to 8.5 ppm that result from the aromatic protons in **2**.

Comment on the refinement of partially occupied H atoms in **1**: Because it was impossible to use a pre-defined constraint or restraint for the refinement of H1A, a tight dfix constraint was employed. The position of the 0.19-occupancy H atom H1B was idealized, its occupancy percentage based on the disorder of the heavier elements.