International Journal of Scientific Research in Science and Technology
© 2018 IJSRST | Volume 4 | Issue 8 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X

Characterization Cathrochelates of Iron (II)

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ABSTRACT

The infrared spectra of complex with legends derived from dimenthylglyoxime and cyclohexanedion dioxide have been reported by the diphenylglyoxime complete€€the new complexes synthesized for this study possess infrared spectra that are virtually identical with dose of the previously reported complexes except for the changes expected from the varied boron substituent, the most dramatic of these being the intense boron hydrogen stretchy at 2490 cm-1 for [Fe (NOX)3 (BH)2] and 2495 cm-1 for [Fe (DMG)3(BH)2]. The UV –visible spectra of the complexes were dominated by an intense (€ 17000L/ (mol.cm)) charge transfer band centered at 22.5×10^{3} cm^{-1} . The position of the charge transfer band was not sensitive to variation in boron substituent.

Keywords – Dimenthylglyoxime, Cyclohexanedione, Diphenylglyoxime

INTRODUCTION

^{1}H NMR signals from the dioxide portion of the clathrochelate legends did not very significantly from complex' i.e cyclohexanedione dioxides had two multiples at ~ 1.8 and ~2.9 ppm, and diphenylglyoxime have multiple at ~7.3 ppm. The ^{1}H resonances of the boron substituent are reported in table 4.1 the methyl substituent's are deshielded by the boron atom and shifted up field to a position very nearly overlapping the Me4 si reverence single. The n-butyl substituent also exhibits an up field shift (0.6) for the protons of the ethylene group attached to the boron atom. The protons of the β and ϒ ethylene's and the terminal methyl appear in their expected position. The ^{1}H resonance of the hydride protons of [Fe (NOX) 3 (BH)2] and [Fe (DMG)3(BH)2] Were not observed. This failure is most likely due large quadruple broadening by the adjacent boron atom.

Compound 4.5 (50 mg, 0.32 mole), 4-bromobenzeneboronic acid (44.2 mg, 0.22 mmol), and anhydrous FeCl2 (13.4 mg, 0.11 mole) were dissolved in Me OH (15 mL) and heated under reflux under an inert atmosphere for 3 h. The reaction mixture was allowed to cool to RT, and the resulting precipitates were isolated by filtration, washed with MeOH and diethyl ether, and dried under vacuum to yield a brown powder (62 mg, 68%).1H NMR (400 MHz, Chloroform-d) δ 1.02 (d, J = 6.4 Hz, 9H, CH3), 1.37 (tq, J = 12.5, 5.4 Hz, 3H, CH), 1.46 (s, 6H, CCH2CH2), 2.26 (dd, J = 18.8, 10.7 Hz, 3H, CCH2CH2), 2.66 (ddd, J = 18.7, 11.6, 6.1 Hz, 3H, –CCH2CH2), 3.16 – 3.06 (m, 4H, CCH2), 7.40 (q, J = 1.9 Hz, 2H, Ar-CH), 7.50 (p, J = 1.7 Hz, 4H, Ar-CH); 13C NMR (CDCl3, 101 MHz, TMS) δ 21.1 (CH3), 25.4 (CH), 28.6 (CCH2CH2), 29.7 (CCH2CH2), 34.0 (CCH2), 122.4 (C-Br), 133.4 (Ar-CH), 151.8 (N-C), 152.1 (N-C), (C-B not detected). All attempts to record a HRMS failed.

Synthesis of complex 4.8:
Compound 4.5 (100 mg, 0.64 mmol), pyridylbenzeneboronic acid (51.6 mg, 0.42mmol), and anhydrous FeCl2 (27 mg, 0.22 mmol) were dissolved in MeOH (15 mL) and heated under reflux under an inert atmosphere for 3 h. The reaction mixture was allowed to cool to RT, and the resulting precipitates were isolated by filtration, washed with MeOH and diethyl ether, and dried under vacuum to yield a brown powder (84 mg, 56%).1H NMR (400 MHz, Chloroform-d) δ 1.10 (d, J = 6.4 Hz, 9H, CH3), 1.5 (tq, J = 12.5, 5.4 Hz, 3H, CH), 1.46 (s, 6H, CCH2CH2), 2.43 (dd, J = 18.8, 10.7 Hz, 3H, CCH2CH2), 2.79 (ddd, J = 18.7, 11.6, 6.1 Hz, 3H, –CCH2CH2), 3.23 – 3.08 (m, 4H, CCH2), 8.04 (q, J = 1.9 Hz, 2H, Ar-CH), 8.83 (p, J = 1.7 Hz, 4H, Ar-CH); 13C NMR (CDCl3, 101 MHz, TMS) δ 20.82 (CH3), 25.34 (CH), 28.36 (CCH2CH2), 29.42 (CCH2CH2), 33.87 (CCH2), 126.9 (CH-CB), 146.9 (CH-N), 152.28 (C-NO). (C-B not detected). HRMS (ESI TOF) m/z calcd for C31H40B2FeN8O6 [M-2H]2+ 349.1303, found 349.1320.

In order to prepare polymeric networks based on din clear clathrochelate complexes, we have performed polycross-coupling reactions of 2.6 with 1,4-benzenediboronic acid or 4,4'-biphenyldiboronic acid, respectively.

The polymers P-7 and P-8 were obtained by heating the reaction mixtures at 110 °C for 12 h (Scheme 4.3). As catalyst precursor, we have employed Pd (PPh3)4 (10 mol% with respect to the bubonic acid) in combination with K2CO3 as base. A molar ratio of 3:1 between the dioramic acid and the brominates clathrochelate was found to give polymers with the highest porosity. The utilization of 1,4-dioxane:H2O (4:1) as solvent was found to be advantageous. Most likely, the excess of bubonic acid is needed to compensate for protodeboronation reactions, as in the case of P-1 and P-2. The covalent linkage of the clathrochelates via phenylene and diphenylene spacers is expected to give large macrocyclic structures if fully connected 3D networks are formed. The preparation of polymers 5.1-5.4 resembles a standard MOF synthesis, because metal-ligand interactions mediate network formation. However, it is worth noting a crucial difference: clathrochelate complexes are kinetically and thermodynamically very stable. Hence, they resemble more a normal organic link than a coordination complex. One should also note that the cleavage of a clathrochelate link would require breaking a covalent bond, whereas MOFs can be cleared by rupture of metal-legend interactions.

It is worth noting that the bubonic acid, the dioxide and FeCl2 were used in a ratio of 1:3:6 respectively, because a screening revealed that the resulting polymers have a higher porosity than those prepared with the 'ideal' stoichiometry of 1:1.5:4.5.

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