Supplementary Material (ESI) for Chemical Communications

Supplementary Experimental Details

Synthesis of **1**

Hmpo (0.196 g, 2 mmol) and ^{t}butylbenzoic acid (0.376 g, 2 mmol) were mixed in methanol (50 cm^3) and added to an aqueous solution of nickel (II) tetrafluoroborate (50% b/w, 0.929g, 2 mmol). The light apple green solution was stirred for 5m. before addition of sodium methoxide solution (4cm^3, 0.5 mol/dm^3, 2 mmol) and refluxing for 24h. The solvent was then removed *in vacuo* leaving a lime green solid that was dissolved in ethyl acetate (25 cm^3), from which crystals of **8** grew over ten days, that were suitable for X-Ray diffraction from a synchrotron source. Yield, 65mg, 7% by % Ni. Elemental analysis: Calculated (found): C 49.63 (48.76); H 5.34 (5.33); N 7.12 (7.07); F 5.23 (6.19), Na 1.59 (1.60); Ni 16.17 (15.81).

Synthesis of **2**

Hmpo (0.196 g, 2 mmol) and ^{t}butylbenzoic acid (0.376 g, 2 mmol) were mixed in methanol (50 cm^3) and added to an aqueous solution of nickel (II) tetrafluoroborate (50% b/w, 0.929 g, 2 mmol). The light apple green solution was stirred for 5m. before addition of sodium methoxide solution (4 cm^3, 0.5 mol/dm^3, 2 mmol) and excess sodium azide (0.65g, 10mmol), which turned the solution notably darker and further stirring for 72h. The solvent was then removed *in vacuo* at room temperature leaving a green solid that was dissolved in ethyl acetate (25 cm^3), and filtered to leave an apple green solution. From this solution crystals of **12** grew over a period of one week, that were suitable for X-Ray diffraction from a synchrotron source. Yield, 47 mg, 7% by % Ni, . Microanalysis suggests that some ethyl acetate is lost in powder form, and that only four molecules remain. Elemental analysis for the molecule without these four ethyl acetate molecules $C_{67}H_{101}N_{56}Na_2Ni_8O_{20}$: Calculated (found): C 31.85 (31.51); H 4.03 (3.94); N 31.05 (29.99).

Synthesis of **3**

Hmpo (0.196 g, 2 mmol) and benzoic acid (0.376 g, 2 mmol) were mixed in methanol (50 cm^3) and added to an aqueous solution of nickel (II) tetrafluoroborate (50% b/w, 0.929 g,

2 mmol). The light apple green solution was stirred for 5m. before addition of sodium methoxide solution (4 cm^3, 0.5 mol/dm^3, 2 mmol) and excess sodium azide (0.65 g, 10 mmol), which turned the solution notably darker and further stirring for 72h. The solvent was then removed *in vacuo* at room temperature leaving a lime green solid that was dissolved in ethyl acetate (25 cm^3), and filtered to leave an apple green solution. From this solution crystals of **13** grew over a period of one week, that were suitable for X-Ray diffraction from a synchrotron source. Yield, 83 mg, 13% by % Ni. Microanalysis indicates that the terminal ethyl acetates are lost in powder form and replaced by water molecules. Elemental analysis for replacement with water molecules as $C_{54}H_{82}N_{56}Na_2Ni_8O_{22}$: Calculated (found): C 27.22 (26.72); H 3.47 (3.36); N 32.91 (32.98).