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Water-soluble bis(4′-[2,2,2-tris(hydroxymethyl)ethoxy]-2,2′:6′,2″-terpyridine)metal complexes

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ABSTRACT

A series of homoleptic metal complexes containing the pentaerythritol-functionalized ligand **1** (4′-(2,2,2-tris(hydroxymethyl)ethoxy)-2,2′:6′,2″-terpyridine) has been synthesized. In MeOH and under microwave conditions, the 2,2,2-tris(hydroxymethyl)ethoxy substituent is cleaved and replaced by a methoxy group originating from the solvent. This has been confirmed from the single crystal structure of $[Zn(\mathbf{2})_2][PF_6]_2$ (**2** = 4′-methoxy-2,2′:6′,2″-terpyridine). The complexes $[Zn(\mathbf{1})_2][OAc]_2$, $[Fe(\mathbf{1})_2]Cl_2$ and $[Co(\mathbf{1})_2][PF_6]_2$ were therefore prepared under mild conditions; $[Co(\mathbf{1})_2][PF_6]_2$ readily oxidizes to $[Co(\mathbf{1})_2][PF_6]_3$; the conversion of the paramagnetic $[Co(\mathbf{1})_2]^{2+}$ to diamagnetic $[Co(\mathbf{1})_2]^{3+}$ is readily monitored by ^{1}H NMR spectroscopy. The homoleptic complexes are hygroscopic and are highly soluble in water; the most soluble is $[Zn(\mathbf{1})_2][OAc]_2$ (71 mmol dm^{-3}). Structural data for **1**, $[Zn(\mathbf{1})_2][PF_6]_2$, 4{$[Zn(\mathbf{1})_2][PF_6]_2$}·3MeCN, $[Zn(\mathbf{1})(OAc\text{-}O)_2]$·2MeOH and 2{$[Co(\mathbf{1})_2][PF_6]_3$}·1.5MeCN·1.5$H_2O$ confirm that dominant packing forces involve hydrogen bonds between pendant 2,2,2-tris(hydroxymethyl)ethoxy units.

1. Introduction

In the next 50 years, materials chemists will be increasingly challenged with addressing the anticipated increase in global demand for energy against a background of diminishing fossil fuels, social and political pressure to reduce the reliance on nuclear power and legislative obligations to minimize the release of greenhouse gases [1]. Many strategies are currently under investigation and an attractive closed cycle involves the combination of the splitting of water into dihydrogen and dioxygen using the energy from solar photons [2–5] followed by the exothermic formation of water in a fuel cell [6] or the conversion into compounds in which the chemical energy is stored (chemical hydrogen storage) [7–14].

Water cannot be directly split into dihydrogen and dioxygen by means of visible light, and a photocatalyst or photoelectrochemical catalyst is required [15–21]. Both homogeneous [22–25] and heterogeneous catalysts [15] are of interest and we have concerned ourselves with the design of ruthenium complexes for use as homogeneous photocatalysts. Typical photocatalysts are based upon $\{Ru^{II}(bpy)_3\}$ (bpy = 2,2′-bipyridine) or $\{Ru^{II}(tpy)_2\}$ (tpy = 2,2′:6′,2″-terpyridine) scaffolds. Homogeneous photocatalysts for water splitting should be water soluble and conventional strategies for solubilising intrinsically hydrophobic cations with oligopyridine ligands rely upon the use of chloride or sulfate salts, the former being inherently unsuitable for application in oxidative conditions. We have previously described the preparation and utilization of the hydrogensulfate salts $[Ru^{II}(Mepytpy)_2][HSO_4]_4$ (Mepytpy = 4′-(4-*N*-methylpyridinio)-2,2′:6′,2″-terpyridine, Scheme 1) as co-catalysts for water oxidation [26] as well as the development of water-soluble sulfonated ligands for the solubilization of $\{Ru^{II}(bpy)_3\}$ derivatives [27]. In unrelated work we have investigated bpy and tpy ligands functionalized with mono- and polysaccharides and commented upon their high water solubility [28–33]. Although saccharides are unsuitable for use as ligands in water splitting reactions owing to their facile oxidation, we considered the investigation of other polyhydroxylated ligands and now describe preliminary studies of the coordination chemistry of the pentaerythritol-functionalized ligand **1** [34].

2. Experimental

2.1. General

Bruker Avance III-400, Avance III-500, or Avance III-600 NMR spectrometers were used to record ^{1}H and ^{13}C NMR spectra, and chemical shifts were referenced to residual solvent peaks with respect to δ(TMS) = 0 ppm. Solution absorption spectra were recorded on an Agilent 8453 spectrophotometer, and FT-IR spectra of solid samples on a Shimadzu 8400S instrument with Golden Gate accessory. Electrospray ionization (ESI) mass spectra were measured using a Bruker esquire 3000^{plus} mass spectrometer. A Biotage Initiator 8 reactor was used for the syntheses under microwave

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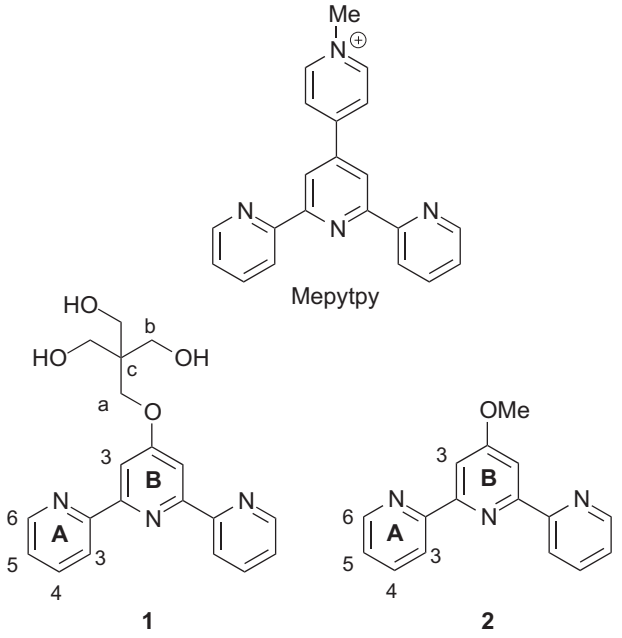

Scheme 1. Structures of mepytpy and ligands **1** and **2**, with labeling for NMR spectroscopic assignments.

conditions. TGA-MS measurements were carried out using a Mettler Toledo TGA/SDTA851[e] with Pfeiffer Vacuum Thermostar™. Ligand **1** was prepared according to the literature method [34].

2.2. $[Zn(\mathbf{2})_2][PF_6]_2$

$Zn(OAc)_2{\cdot}2H_2O$ (9.00 mg, 41.0 μmol) was added to a solution of **1** (30 mg, 82.0 μmol) in MeOH (4 cm^3) and the mixture was heated in the microwave reactor for 60 min at 120 °C. Excess aqueous NH_4PF_6 was added and the precipitate collected by filtration, washed with H_2O, and then Et_2O, and dried *in vacuo*. $[Zn(\mathbf{2})_2][PF_6]_2$ was isolated as a white solid (39.7 mg, 45.0 μmol, 91%). ^{1}H NMR (400 MHz, CD_3CN) δ/ppm 8.55 (d, J = 8.1 Hz, 4H, H^{A3}), 8.19 (s, 4H, H^{B3}), 8.12 (t, J = 7.7 Hz, 4H, H^{A4}), 7.76 (d, J = 5.0 Hz, 4H, H^{A6}), 7.37 (m, 4H, H^{A5}), 4.29 (s, 6H, H^{Me}). ESI MS 735.1 $[Zn(\mathbf{2})_2PF_6]^+$ (base peak, calc. 735.1). IR (solid, ν/cm^{-1}) 1439m, 1418s, 1367m, 1232m, 1157s, 1059s, 1036s, 1013s, 906s, 824w, 793w, 746m, 727m, 696m, 660m, 631m, 554w, 488m, 474m, 469m, 455m, 438w, 430m, 405w, 399m, 384m, 380w UV–Vis (MeOH, 1.0×10^{-5} mol dm^{-3}) λ/nm 203 (ε/dm^3 mol^{-1} cm^{-1} 42500), 244 (40100), 273 (30000), 310 (21200), 322 (23700). *Anal.* Calc. for $C_{34}H_{34}F_{12}N_6O_3P_2Zn$ requires: C, 43.58; H, 2.97; N, 9.53. Found: C, 43.22; H, 3.12; N, 9.54%.

2.3. $[Zn(\mathbf{2})_2][OAc]_2$

$Zn(OAc)_2{\cdot}2H_2O$ (28.0 mg, 95.0 μmol) was added to a solution of 4′-methoxy-2,2′:6′,2″-terpyridine (50 mg, 190.0 μmol) in MeOH (5 cm^3) and the mixture was stirred at room temperature for 60 min, after which, the solvent was removed *in vacuo*. $[Zn(\mathbf{2})_2][OAc]_2$ was isolated as a white solid (55.7 mg, 78.5 μmol, 83%). ^{1}H NMR (500 MHz, CH_3OD) δ/ppm 8.75 (d, 4H, H^{A3}), 8.46 (s, 4H, H^{B3}), 8.19 (t, 4H, H^{A4}), 7.85 (d, 4H, H^{A6}), 7.46 (m, 4H, H^{A5}), 4.32 (s, 6H, H^{Me}). ^{13}C NMR (126 MHz, CH_3OD) δ/ppm 173.6 (C^{B4}), 169.3 (C^{B2}), 148.7 (C^{A6}), 144.5 (C^{A2}), 142.3 (C^{A4}), 128.8 (C^{A5}), 124.2 (C^{A3}), 110.8 (C^{B3}), 57.92 (C^{Me}). ESI-MS m/z 386.1 $[M–OAc–\mathbf{2}]^+$ (calc. 386.1), 295.1 $[M–2OAc]^{2+}$ (calc. 295.1). IR (solid, ν/cm^{-1}) 2358s, 1704s, 1575s, 1555s, 1388s, 1229s, 1031m, 1014s, 793w, 668m, 659s, 621m, 552w, 525w, 515w, 511w. UV–Vis (MeOH, 1.0×10^{-5} mol dm^{-3}) λ/nm 203 (ε/dm^3 mol^{-1} cm^{-1} 38200), 244 (34900), 273 (25800), 310 (18500), 335 (21000). *Anal.* Calc. for $C_{36}H_{32}N_6O_6Zn{\cdot}2H_2O$ requires: C, 57.95; H, 4.86; N, 11.26. Found: C, 58.04; H, 4.53; N, 11.03%.

2.4. $[Fe(\mathbf{1})_2]Cl_2$

Anhydrous $FeCl_2$ (17.3 mg, 0.14 mmol) was added to a solution of **1** (100 mg, 0.27 mmol) in EtOH (10 cm^3) and the mixture was stirred at room temperature for 1 h to give a dark purple solution. Solvent was removed *in vacuo* to yield a dark purple solid which was purified on a Sephadex column (LH 20, MeOH). $[Fe(\mathbf{1})_2]Cl_2$ was isolated as a purple solid (85.6 mg, 99.4 μmol, 71%). ^{1}H NMR (500 MHz, CD_3OD) δ/ppm 8.79 (s, 4H, H^{B3}), 8.67 (d, J = 8.1 Hz, 4H, H^{A3}), 7.93 (td, 4H, J = 7.7, 1.5 Hz, H^{A4}), 7.27 (d, J = 5.4 Hz, 4H, H^{A6}), 7.17 (m, 4H, H^{A5}), 4.67 (s, 4H, H^a), 3.91 (s, 12H, H^b). ^{13}C NMR (126 MHz, CD_3OD) δ/ppm 169.7 (C^{B4}), 161.0 (C^{B2}), 159.7 (C^{A2}), 154.0 (C^{A6}), 139.7 (C^{A4}), 128.4 (C^{A5}), 124.7 (C^{A3}), 112.4 (C^{B3}), 69.9 (C^a), 61.8 (C^b), 47.4 (C^c). ESI MS m/z 825.2 $[Fe(\mathbf{1})_2Cl]^+$ (calc. 825.2), 789.3 $[Fe(\mathbf{1})(\mathbf{1}–H)]^+$ (base peak, calc. 789.2), 757.3 $[2(\mathbf{1})+Na]^+$ (calc. 757.3). IR (solid, ν/cm^{-1}) 3597vs, 3310s, 3221vs, 2957vs, 2883vs, 1616m, 1562s, 1483s, 1439m, 1366s, 1225m, 1165vs, 1030m, 1003s, 827m, 785m, 752s, 555m, 463m, 457m, 426w, 415w, 363m, 353w, 343w. UV–Vis (MeOH, 1.0×10^{-5} mol dm^{-3}) λ/nm 204 (ε/dm^3 mol^{-1} cm^{-1} 123800), 244 (66100), 272 (75000), 316 (54000), 362 (7300), 556 (15500). *Anal* Calc. for $C_{40}H_{42}Cl_2FeN_6O_8{\cdot}10H_2O$ requires: C, 48.11; H, 6.24; N, 7.65. Found: C, 47.99; H, 6.05; N, 7.32%.

2.5. $[Zn(\mathbf{1})_2][OAc]_2$

$Zn(OAc)_2{\cdot}2H_2O$ (29.8 mg, 0.14 mmol) was added to a solution of **1** (100 mg, 0.27 mmol) in MeOH (10 cm^3) and the mixture stirred at room temperature for 1 h. Solvent was removed *in vacuo* and the product purified on a Sephadex column (LH 20, MeOH) to yield $[Zn(\mathbf{1})_2][OAc]_2$ as an off-white solid (88.7 mg, 96.6 μmol, 69%). ^{1}H NMR (500 MHz, CD_3OD) δ/ppm 8.76 (d, J = 8.2 Hz, 4H, H^{A3}), 8.50 (s, H^{B3}) 8.19 (td, J = 7.6, 1.7 Hz, 4H, H^{A4}), 7.85 (br, 4H, H^{A6}), 7.46 (m, 4H, H^{A5}), 4.58 (s, 4H, H^a), 3.84 (s, 12H, H^b), 1.87 (s, 6H, H^{AcO}). ^{13}C NMR (126 MHz, CD_3OD) δ/ppm 173.5 (C^{B4}), 152.4 (C^{B2}), 149.6 (C^{A2}), 148.6 (C^{A6}), 142.5 (C^{A4}), 128.6 (C^{A5}), 124.2 (C^{A3}), 111.2 (C^{B3}), 70.1 (C^a), 61.9 (C^b), 47.3 (C^c), 24.2 (C^{AcO}). ESI MS m/z 797.2 $[Zn(\mathbf{1})(\mathbf{1}–H)]^+$ (calc. 797.2), 757.3 $[2(\mathbf{1})+Na]^+$ (base peak, calc. 757.3), 390.2 $[\mathbf{1}+Na]^+$ (calc. 390.1). IR (solid, ν/cm^{-1}) 1439m, 1418s, 1367m, 1232m, 1157s, 1059s, 1036s, 1013s, 906s, 824w, 793w, 746m, 727m, 696m, 660m, 631m, 554w, 488m, 474m, 469m, 455m, 438w, 430m, 405w, 399m, 384m, 380w. UV/VIS (MeOH, 1.0×10^{-5} mol dm^{-3}) λ/nm 203 (ε/dm^3 mol^{-1} cm^{-1} 83800), 245 (68200), 274 (55900), 310 (35100), 322 (36300). *Anal.* Calc. for $C_{44}H_{48}N_6O_{10}Zn{\cdot}11H_2O$ requires: C, 47.34; H, 6.32; N, 7.53. Found: C, 47.99; H, 6.05; N, 7.32%.

2.6. $[Co(\mathbf{1})_2][PF_6]_2$ and $[Co(\mathbf{1})_2][PF_6]_3$

$Co(BF_4)_2{\cdot}6H_2O$ (46.4 mg, 0.14 mmol) was added to a solution of **1** (100 mg, 0.27 mmol) in MeOH (10 cm^3) and the mixture stirred at room temperature under argon for 1 h. An excess of aqueous NH_4PF_6 was then added and the solvent was removed *in vacuo* to give a brown-orange solid (108.3 mg, 0.11 mmol, 80%). After initial analysis of the predominantly cobalt(II) complex was completed, H_2O_2 and activated charcoal were added to fully oxidize the metal to cobalt(III). This was purified on a Sephadex column (LH 20, H_2O) to yield pure $[Co(\mathbf{1})_2][PF_6]_3$ as a yellow-orange solid (65.9 mg, 53.6 μmol, 40%). $[Co(\mathbf{1})_2][PF_6]_2$: ^{1}H NMR (600 MHz, CD_3CN) δ/ppm 112 (br, H^{A6}), 75.5 (s, H^{A3}) 70.6 (s, H^{B3}), 34.6 (s, H^{A5}), 15.27 (s, H^a),