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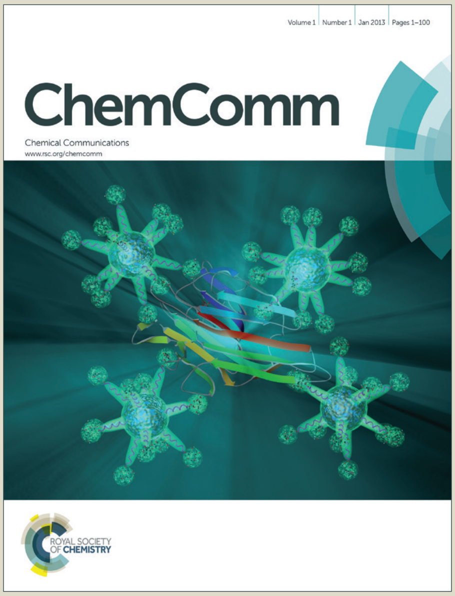

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Photoinduced Water Oxidation Catalyzed by a Double-Helical Dicobalt(II) Sexipyridine Complex †

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A double-helical dicobalt(II) complex $[Co_2(spy)_2](ClO_4)_4$ (spy = 2,2':6',2":6",2"':6"',2"":6"",2""'–sexipyridine) (1) is found to catalyze visible light-induced water oxidation by $[Ru(bpy)_3]^{2+}/Na_2S_2O_8$, with a maximum turnover number of 442. Several lines of evidence suggest that 1 functions as a molecular catalyst and does not produce any CoO_x in water oxidation.

In recent years, there have been intense efforts in developing efficient water oxidation catalysts (WOCs) based on earth abundant metals.[1-14] Water oxidation can provide protons and electrons for the production of renewable fuels.[15,16] A number of cobalt catalysts have recently been found to be efficient catalysts for chemical, electrochemical and photochemical water oxidation. Simple cobalt(II) salts are converted under oxidative conditions to CoO_x cluster which is an excellent WOC.[17] A number of cobalt complexes bearing organic ligands have also been demonstrated to function as precatalysts that decompose to give CoO_x as the real catalyst for water oxidation.[18,19] On the other hand, there are also examples of cobalt complexes that can function as homogeneous, molecular WOCs, including those bearing phthalocyanine,[20] corrole,[21] porphyrin,[22,23] salen[24] and polypyridyl[25-27] and polyoxometalate ligands.[28-31]

All cobalt WOCs reported so far contain at least an aqua ligand or a labile/vacant site that can form an aqua complex in water. Presumably the cobalt aqua catalysts undergo proton-coupled electron transfer to generate cobalt(IV) oxo species: $LCo^{II}\text{-}OH_2 - 2e - 2H^+ \rightarrow LCo^{IV}{=}O \leftrightarrow LCo^{III}\text{-}O\bullet$. The cobalt(IV) oxo species may be the active species, or it may decompose to give CoO_x as the real catalyst.

We recently reported that a cobalt(II) complex bearing a quaterpyridine ligand is a stable and efficient molecular catalyst for both water oxidation and reduction.[25] Inspired by the oxygen evolution centre in photosystem II, which consists of a Mn_4CaO_5 centre,[32] we are interested in designing multimetallic WOCs based on oligopyridine ligands. We report herein an interesting dicobalt WOC, $[Co_2(spy)_2](ClO_4)_4$ (**1**, spy = 2,2':6',2":6",2"':6"',2"":6"",2""'–sexipyridine). This compound has a coordination environment similar to that of $[Co(tpy)_2]^{2+}$ (tpy = 2,2':6',2"-terpyridine); each Co is bound by two strongly chelating tpy fragments and apparently does not have open/labile sites for the formation of an aqua complex. However, **1** is an efficient WOC while $[Co(tpy)_2]^{2+}$ is totally inactive.

$[Co_2(spy)_2](ClO_4)_4$ (**1**) was prepared according to a literature method.[33] The structure of **1** was determined by X-ray crystallography (Fig. 1 and Table S1). The X-ray structure shows the presence of $[Co_2(spy)_2]^{4+}$ cations, which have a double helical structure that is similar to that of $[Zn_2(spy)_2]^{4+}$ and $[Fe_2(spy)_2]^{4+}$.[33,34] The two Co centres adopt distorted octahedral geometry and are bridged by two spy ligands, with each Co centre being coordinated to a tpy fragment of each spy ligand. The Co-N bond distances (2.047-2.225 Å) are longer than those of $[Co(tpy)_2]^{2+}$ (1.882-2.116 Å).[35] The N–Co–N bite angles of the tpy fragments (N1–Co1–N3 and N4–Co2–N6) are 150.50° and 151.45°, respectively, which deviate significantly from the ideal value of 180° for an octahedral complex, indicating that the complex is highly distorted.

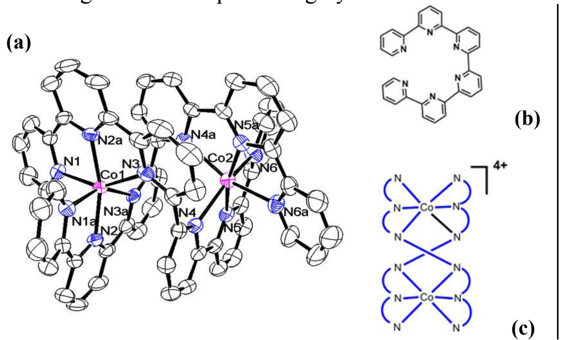


Fig. 1 (a) ORTEP diagram of $[Co_2(spy)_2]^{4+}$. Hydrogen atoms have been omitted for clarity. Operators for generating equivalent atoms are –x+1/2, y, –z+1. (b) Schematic diagram of spy ligand. (c) Schematic diagram of $[Co_2(spy)_2]^{4+}$.

The complex is stable in water for >10 d at room temperature at pH 5–9, as monitored by UV/Vis spectrophotometry (Fig. S1). It is, however, unstable at low pH; when dissolved in 0.1 M HNO_3, free spy ligand was readily formed as a precipitate.

The efficacy of **1** as a WOC was initially investigated by using $[Ru(bpy)_3](ClO_4)_3$ (bpy = 2'2-bipyridine) as the oxidant at pH 8 in borate buffer. Oxygen evolution (determined by Clark electrode) readily occurred upon adding $[Ru(bpy)_3](ClO_4)_3$ to **1**, with a turnover number (TON) of 56 and a maximum turnover frequency (TOF) of 0.8 s^{-1} (Fig. 2A). In the absence of the cobalt catalyst, a small amount of O_2 was also detected, which is due to background oxidation of water by $[Ru(bpy)_3]^{3+}$.[8,14,25,36] Notably $[Co(tpy)_2](ClO_4)_2$, which has a similar coordination environment to each cobalt in **1**, showed no catalytic activity.

Both the TON and TOF were found to increase as the pH of solution was increased (Fig. 2B), in accordance with water oxidation being thermodynamically more favorable as the pH is increased. The TOF increases from 0.8 s^{-1} to 1.9 s^{-1} on going from pH 8.0 to 8.5. However, **1** is inactive at pH ≤7.6.

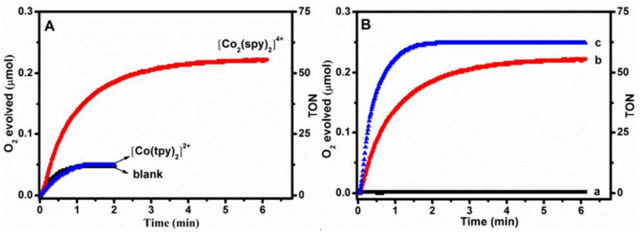


Fig. 2 Plots of oxygen evolution *vs* time for chemical water oxidation by $[Ru(bpy)_3](ClO_4)_3$ (0.7 mM): (A) 0.5 μM $[Co(tpy)_2](ClO_4)_2$ or $[Co_2(spy)_2](ClO_4)_4$ at pH 8.0 in aqueous borate buffer (15 mM, 8.25 mL) at 23 °C. (B) Effects of pH: a) 7.6, b) 8.0, c) 8.5. $[Co_2(spy)_2](ClO_4)_4$ = 0.5 μM.

The amount of O_2 increases when the concentration of the Co(II) catalyst as well as the Ru(III) oxidant increase (Fig. 3A and 4A). The initial rate of O_2 evolution also increases when the concentration of Co(II) catalyst increases, but it reaches saturation at [Co(II)] ca. 1 μM. On the other hand, the initial rate increases linearly with [Ru(III)]. The saturation behaviour at high [Co(II)] may be due to reorganization of the cobalt catalyst being the rate-limiting step (see below).

Attempts to detect any cobalt intermediate by UV/Vis spectrophotometry were unsuccessful, the spectrophotmetric changes upon adding $[Ru(bpy)_3]^{3+}$ to **1** were dominated by the intensely absorbing $[Ru(bpy)_3]^{2+}$ product (Fig S2).

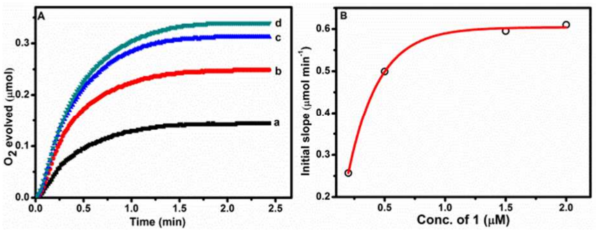


Fig. 3 (A) Plot of oxygen evolution *vs* time for catalytic water oxidation by $[Ru(bpy)_3](ClO_4)_3$ (0.7 mM) at pH 8.5 and 23 °C. Effects of $[Co_2(spy)_2(ClO_4)_4]$: a) 0.2 μM, b) 0.5 μM, c) 1.5 μM, d) 2.0 μM. (B) Plot of initial rate *vs* [**1**].

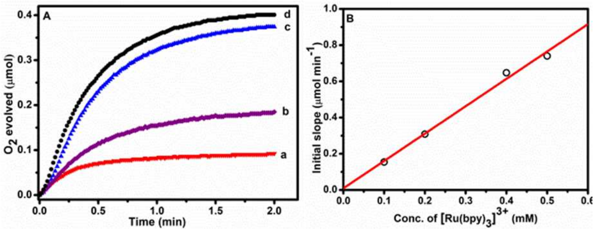
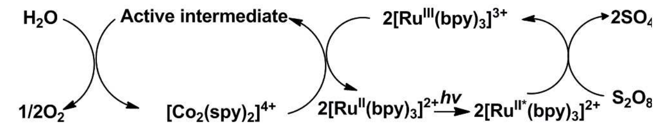


Fig. 4 (A) Plots of oxygen evolution *vs* time for catalytic water oxidation catalyzed by $[Co_2(spy)_2](ClO_4)_4$ (4 μM) at pH 8.5 and 23 °C. Effects of concentration of $[Ru(bpy)_3](ClO_4)_3$: a) 0.1 mM, b) 0.2 mM, c) 0.4 mM and d) 0.5 mM. (B) Plot of initial rate *vs* $[Ru^{III}]$.

1 also catalyzes visible light-induced water oxidation using $[Ru(bpy)_3](ClO_4)_2$ as the photosensitizer (PS)[37] and $Na_2S_2O_8$ as the sacrificial oxidant,[38] at pH 7.5 - 9 in borate buffer. The photocatalytic cycle is shown in Scheme 1. Oxygen evolved was determined by GC-TCD. Control experiments showed that all three components, i.e. the cobalt catalyst, $[Ru(bpy)_3]^{2+}$ and $Na_2S_2O_8$ are needed for water oxidation. Under the conditions shown in Fig. 5, a TON of 150 could be obtained after irradiation for 3h. Interestingly, as in the case of chemical water oxidation, $[Co(tpy)_2]^{2+}$, as well as $[Co(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine), showed no catalytic activity.



Scheme 1

The effects of [PS] and $Na_2S_2O_8$ on photocatalytic water oxidation were investigated. The amount of oxygen first increased and then decreased with $[Ru(bpy)_3]^{2+}$ (Fig. 6A). A similar trend was observed for $Na_2S_2O_8$ (Fig. 6B). These results can be attributed to non-O_2 productive decomposition reactions between $Na_2S_2O_8$ and $[Ru(bpy)_3](ClO_4)_2$.[39,40]

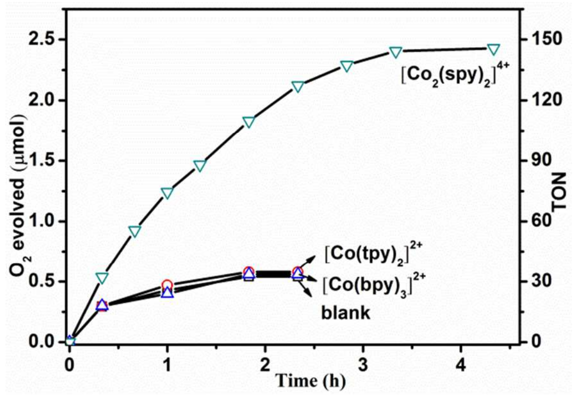


Fig. 5 Plots of oxygen evolution *vs* time for photoinduced (Xe lamp, 500 W, λ = 457 nm) catalytic water oxidation at 23 °C and pH 8.5 (8.25 mL of 15 mM borate buffer). $[Ru(bpy)_3](ClO_4)_2$ = 0.1 mM, $Na_2S_2O_8$ = 12 mM, Co catalyst = 2.0 μM.

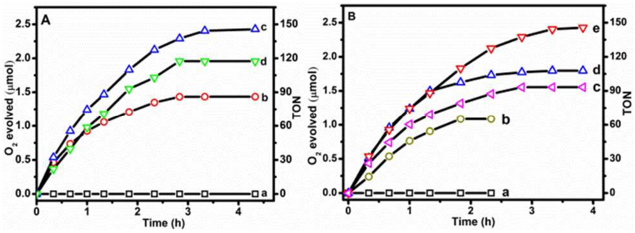


Fig. 6 Plots of oxygen evolution vs time for photoinduced water oxidation by **1** at pH = 8.5 and 23 ºC. A) Effects of $[Ru(bpy)_3^{2+}]$: a) 0, b) 0.05, c) 0.1 and d) 0.15 mM. **1** = 2.0 μM, $Na_2S_2O_8$ = 12 mM. B) Effects of $[Na_2S_2O_8]$: a) 0, b) 4, c) 8, d) 12 and e) 20 mM. 1 = 2.0 μM, $[Ru(bpy)_3]^{2+}$ = 0.1 mM.

The effects of catalyst concentration on O_2 evolution have also been investigated. O_2 evolution increases steadily with [**1**] from 0.2 to 2.0 μM (Fig. 7). A maximum TON of 442 was obtained at [**1**] = 0.2 μM after irradiation with visible light for 3 h. The intial rate of O_2 production also increases with [1].

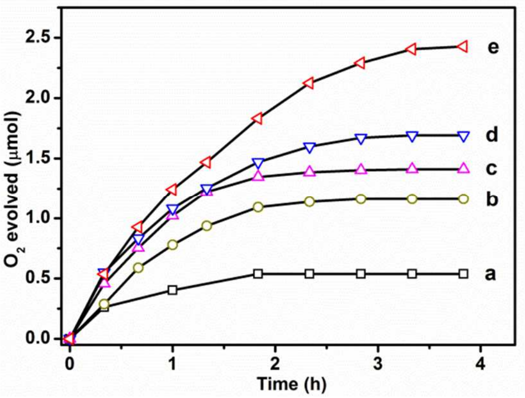


Fig. 7 Plots of oxygen evolution vs time for photoinduced water oxidation by **1** at pH = 8.5 and 23 ºC. Effects of [**1**]: a) 0, b) 0.2, c) 0.5, d) 1.0 and e) 2.0 μM. $[Ru(bpy)_3]^{2+}$ = 0.1 mM, $Na_2S_2O_8$ = 12 mM.

Several lines of evidence indicate that **1** functions as a molecular catalyst and does not decompose to CoO_x in photocatalytic water oxidation. First, dynamic light scattering (DLS) was used to detect any particles formed during water oxidation. No particles were observed (Fig. S3) after 1 h irradiation of a solution containing **1** (50 μM), $[Ru(bpy)_3](ClO_4)_2$ (0.5 mM) and $Na_2S_2O_8$ (10 mM). The pH of the solution decreased from 8.5 to 7.8 after irradiation; at this pH range any CoO_x formed would remain insoluble and detectable. If $Co(NO_3)_2$ was used under the same conditions, particles of 350 nm mean size were observed (Fig. S4).

The relative amount of soluble cobalt species that remains in solution after photocatalysis was also analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Table S3). After photocatalysis, the solution was centrifuged at 13,000 rpm for 30 min. and the cobalt content of the supernatant solution was analyzed by ICP-AES. It was found that 98.1(±1%) of soluble cobalt was present after photocatalysis when **1** was used as catalyst, suggesting an upper limit of 3% cobalt catalyst was converted to an insoluble form. On the other hand, when $Co(NO_3)_2$ was used as catalyst, only 3.1(±1%) cobalt remained in solution, in accordance with Co^{2+}(aq) being converted to CoO_x as the real catalyst. To further confirm that oxygen evolution was not caused by ≤3 % of free cobalt(II) ions generated from **1**, photocatalytic water oxidation by **1** was carried out in the presence of 9% of tpy ligand, which would scavenge ≤3% Co^{2+}(aq) ions present. It was found that oxygen evolution was lowered by around 10%, which was probably due to oxidation of the free tpy ligand (Fig. S5). Independent experiments showed that the water oxidation activity of Co^{2+}(aq) was completely quenched by 3 mol equiv. of tpy. These results strongly suggest that **1** functions as a molecular WOC.

The nature of the cobalt species present in the solution after photocatalytic water oxidation was also investigated by electrospray ionization mass spectrometry (ESI/MS). Fig. 8 shows that besides the ruthenium species $\{[Ru^{II}(bpy)_3](ClO_4)\}^+$ and $[Ru^{II}(bpy)_3]^{2+}$, the cobalt species $\{[Co_2^{III}(spy)_2](SO_4)_2\}^{2+}$ was also observed at m/z 619. No free ligand $[Hspy]^+$ (m/z = 465) or cobalt aqua ions $[Co(H_2O)_6]^{2+}$ (m/z = 167) were found at m/z between 50 and 1000. These results indicate that **1** is a stable WOC.

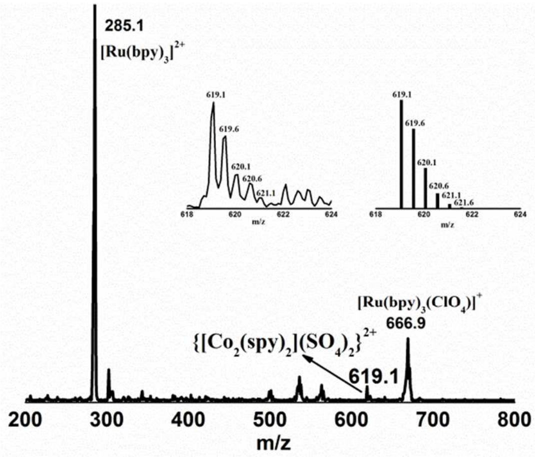


Fig. 8 ESI/MS of a solution of **1** (0.1 mM) with $[Ru(bpy)_3](ClO_4)_2$ (0.5 mM) and $Na_2S_2O_8$ (10 mM) at pH = 8.5 in borate buffer (15 mM) after irradiation with light at λ = 457 nm for 3 h at 23 ºC. The solution was diluted with 3 vol. of CH_3CN before electrospraying. Insets show the expanded (left) and simulated (right) isotopic mass distributions.

All the above results are consistent with **1** being an efficient and stable molecular WOC, with a maximum TOF of 1.9 s^{-1} in chemical water oxidation and a maximum TON of 422 in visible light-induced water oxidation. The TOF is much lower than that of the cobalt POM complex $Na_{10}[Co_4(H_2O)_2(VW_9O_{34})_2].35H_2O$ (TOF>1 × 10^3 s^{-1}) reported recently by Hill and coworkers,[31] but is comparable to other cobalt WOC. The TON is, however, among the highest of the cobalt WOC. It is an intriguing observation that **1** can function as an active WOC, since apparently it has no labile sites for forming an aqua complex, while $[Co(tpy)_2]^{2+}$ and $[Co(bpy)_3]^{2+}$, which have similar coordination environment, are completely inactive WOCs. One possibility is because of the more open structure of **1**, formation of a seven-coordinate aqua/hydroxo/oxo species is feasible, as in a number of Ru WOCs.[41,42] However, attempts to locate a seven-coordinate species from **1** by DFT calculations were unsuccessful. Hence we propose that since **1** has a much more distorted structure with longer Co-N distances than those of $[Co(tpy)_2]^{2+}$, a Co-N bond may be cleaved and replaced by Co-OH_2 under oxidative conditions.

In conclusion, we have reported an unusual case of water oxidation catalyzed by a coordinatively saturated double-helical dicobalt(II) sexipyridine complex. Our results suggest that oligopyridines are potentially useful ligands for the construction of active, multinuclear molecular WOCs, because of their ability to bridge and chelate strongly to transition metals.

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Notes and references

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† Electronic Supplementary Information (ESI) available: experimental details, X-ray crystallographic data (CCDC 1019645) and catalysis results. See DOI: 10.1039/b000000x/

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