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Synthesis of a $Ru(bpy)_3$-type complex linked to a free terpyridine ligand and its use for preparation of polynuclear bimetallic complexes

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Abstract

A terpyridine ligand has been covalently linked to a $Ru(bpy)_3$ complex via an amide bond. By using this functionalized terpyridine ligand, a series of multinuclear bimetallic complexes have been synthesized and characterized. One of these complexes has the structure of di-μ-oxo-bridged Mn dimer. EPR spectra of this complex showed that, depending on the procedure for the preparation, the oxidation states of the Mn dimer is either a $Mn_2^{III,IV}$ dimer or a mixture of this and $Mn_2^{IV,IV}$ dimer. Water oxidation catalyzed by this complex has been performed.

Keywords: Water oxidation; Artificial photosynthesis; Photosystem II; Ruthenium–manganese; Electrochemistry; EPR; Homogeneous catalysis

1. Introduction

In the oxygen evolving photosynthetic organisms, cyanobacteria, plants and algae, a cluster of four manganese ions in Photosystem II (PSII) is responsible for the oxidation of water, a process that provides the electrons needed for the photo-catalyzed reduction of carbon dioxide to biomass. Recently, the X-ray structure of the PSII complex has been resolved by two groups to medium-high resolution [1,2]. The structure at this resolution resolves the problem of the localization of the Mn-cluster in PSII but did not resolve the molecular structure of the Mn-cluster, which remains one of the major unresolved structures among the large natural redox enzymes. The same holds for the mechanism of water oxidation that is not fully understood [3,4]. EPR and XANES studies show that the Mn ions mainly take high oxidation states during the oxygen evolving cycle and the most preferred oxidation state for the so-called S_2 state is $Mn^{III}Mn_3^{IV}$ [4].

Attempts to mimic the fascinating reaction of PS II are many [5,6]. Despite extensive studies, only a few synthetic Mn-complexes have been reported to be active in catalytic water oxidation under homogeneous conditions [7–13], and the most stable of these water oxidizing Mn-complexes is $[(terpy)(H_2O)Mn^{III}(O)_2Mn^{IV}(OH_2)(terpy)](NO_3)_3$ (**1**). So far the water oxidation has only been shown to work with an oxygen transfer reagent. In our earlier work, we have been heavily engaged in studying systems which permit electron transfer from Mn-complexes that are covalently linked to a photosensitizer $Ru(bpy)_3$ complex [14–21]. In an attempt to develop a photochemically driven water oxidation system, we have therefore set out to synthesize complexes where a $Ru(bpy)_3$-structure is linked to a Mn-containing structure such as **1**. Here we report on the attempts to synthesize one such complex **3**. The primary goal was to synthesize complex **2**, which should provide the desired site for coordination of manganese. The subsequent Mn-oxidation to the mixed valence complex **3** was then carried

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out in a procedure similar to that used in the preparation of **1**. Complex **2** should also be useful for the preparation of other types of mixed metal complexes, which contain a Ru(bpy)$_3$-based photo-electron donor. Although a few similar complexes have been reported in the literature [22–25], new complexes of this type clearly are of general interest.

2. Experimental

2.1. General

Dimethylformamide (DMF) was distilled from CaH$_2$. All other reagents and solvents were purchased as reagent grade and used without further purification. NMR spectra were recorded on a Varian (300 or 400 MHz) spectrometer.

2.2. Photophysics

The emission and absorption measurements were performed at room temperature in acetonitrile of spectroscopic grade. The absorption spectra were recorded on an HP 8453 diode array spectrophotometer, and the emission spectra were recorded using a flourolog II system. The time resolved measurements where recorded using a time-correlated single-photon counting setup described previously [26,27].

EPR spectra were recorded on a Bruker E580-ELEXSYS spectrometer equipped with an Oxford 900 liquid helium cryostat. Stable low working temperature (<10 K) was obtained by an ITC 503 temperature controller.

2.3. Electrochemistry

Cyclic voltammetry and differential pulse voltammetry were carried out in a three-compartment cell by using a glassy carbon disk working electrode, a platinum wire as the counter electrode and a Ag/Ag$^+$ (10 mM AgNO$_3$ in CH$_3$CN) reference electrode. The experiments were carried out in dry acetonitrile with 0.1 M tetrabutyl ammonium hexafluorophosphate.

2.4. Oxygen measurements

Oxygen evolution was carried out with a Hansatech oxygen electrode in an airtight chamber connected to a computer-controlled oxygraph. All solutions were degassed with argon until free of oxygen. In a typical experiment, an aliquot (50 μl) of a solution of oxone (29 mM) was added with a syringe to a 0.2 mM solution of complexes **1**, **2** or **3** (generated in situ from **2** and MnOAc) in 0.1 M acetate buffer (pH 4.4)/acetonitrile (9:1). All experiments were followed by a reference experiment without complexes **1**, **2** or **3** to ensure that the added oxone solution did not give a rise to oxygen in the chamber.

2.5. N-[4-(2,2′:6′,2″-Terpyridine-4′-yl-benzyl)]-isoindole-1, 3-dione (**5**)

A suspension of 4′-(bromomethyl-phenyl)-2,2′:6′,2″-terpyridine (**4**) (4.0 g, 0.010 mol) and potassium phthalimide (3.3 g, 0.018 mol) in dry dimethylformamide (100 mL) was heated under argon at 80 °C for 3 h. The solution was cooled to room temperature, diluted with CHCl$_3$ (100 mL), and filtered. The white precipitate was washed with CHCl$_3$. The combined filtrate was washed with water (100 mL) and the aqueous phase was extracted with CHCl$_3$ (2× 50 mL). The combined organic phase was washed with 100 mL NaOH (0.1 M) and water (2× 100 mL). The solvent was evaporated until a white solid started to precipitate. Et$_2$O was added to get complete precipitation. The solid was collected by filtration, washed with Et$_2$O and dried to give 4.5 g (96%) of product **5**. ^{1}H NMR (δ, CDCl$_3$): 4.92 (s, 2H, PhtCH$_2$ph–), 7.32–7.36 (m, 2H, Py-H), 7.57 (d, J = 8.2 Hz, 2H, Ph-H), 7.57 (d, J = 8.2 Hz, 2H, Ph-H), 7.69–7.73 (m, 2H, PyH), 7.84–7.88 (m, 6H, Ph-H and Pht-H), 8.62–8.65 (m, 2H, Py-H), 8.68–8.72 (m, 4H, Py-H).

2.6. 4-(2,2′:6′,2″-Terpyridine-4′-yl-benzyl)-amine (**6**)

Compound **5** (2.0 g, 4.3 mmol) was dissolved in a mixture of ethanol (30 mL) and CHCl$_3$ (40 mL). Hydrazine (0.8 g) was added and the resulting solution was heated under argon at 65 °C for 4 h. The reaction mixture was cooled and the white solid that formed during reaction was filtered off. The filtrate was evaporated and the solid dried to give 1.2 g (79%) of product **6**. ^{1}H NMR (δ, CDCl$_3$): 3.97 (s, 2H, PhCH$_2$N–), 7.33–7.37 (m, 2H, Py-H), 7.46 (d, J = 8.2 Hz, 2H, Ph-H), 7.84–7.89 (m, 4H, Ph-H and Py-H), 8.64–8.67 (m, 2H, Py-H), 8.71–8.74 (m, 4H, Py-H). Elemental analysis: found: C, 75.15; H, 5.45; N, 15.91; calcd. for **6** × 0.75H$_2$O: C, 75.12; H, 5.58; N, 15.93.

2.7. Ruthenium-terpyridine complex (**2**)

A solution of Ru(bpy)$_2$(4-Me-4′-COOH-2,2-bpy)(PF$_6$)$_2$ (0.25 g, 0.27 mmol) in 20 mL SOCl$_2$ was heated at reflux for 2 h under argon. Excess of SOCl$_2$ was removed under reduced pressure. The resulting solid was immediately dissolved in 6 mL CH$_3$CN and 0.4 mL triethyl amine and added to a solution of **6** (0.14 g, 0.41 mmol) in 6 mL dry CH$_2$Cl$_2$. The resulting solution was heated at reflux for 2 h under argon and left at 40 °C over night. The solvent was removed under reduced pressure and the resulting solid was purified on a column of silica gel with CH$_3$CN/H$_2$O/KNO$_3$(sat) (90:7.5:2.5) as eluent. The fractions containing the product were identified collected and the solvent was removed under reduced pressure. The remaining solid was dissolved in a small amount of MeOH/acetone (1:1) and NH$_4$PF$_6$ in water was added until a precipitate was formed. The precipitate was filtered off, washed with water and dried in a desiccator. The product was re-crystallized from EtOH to give 0.20 g of the product. Electrospray ionization mass spectrometry (ESI-MS) gave a monocharged peak at *m/z* 1093 $[M - PF_6^-]^+$ and a doubly charged peak at *m/z* 474 $[M - 2PF_6^-]^{2+}$. Elemental analysis: found: C, 47.36; H, 3.25; N, 10.17; calcd. for **3** × $0.75KPF_6$: C, 47.31; H, 3.09; N, 10.21. ^1H NMR (δ, CD_3CN): 2.54 (s, 3H, $-CH_3$), 4.70 (d, *J* = 5.6 Hz, 2H, $PhCH_2N-$), 7.26 (d, *J* = 5.6 Hz, 1H, Py-H), 7.38–7.46 (m, 4H, Py-H), 7.58 (d, *J* = 6 Hz, IH, Py-H), 7.64 (d, *J* = 8.2 Hz, 2H, Ph-H), 7.68–7.75 (m, 7H, Py-H), 7.87 (d, *J* = 6 Hz, 1H, Py-H), 7.98 (d, *J* = 8.2 Hz, 2H, Ph-H), 8.01–8.1 (m, 5H, 1N-H, 4Py-H), 8.28 (t, *J* = 7.6 Hz, 2H, Py-H), 8.47–8.52 (m, 5H, Py-H), 8.68–8.74 (m, 4H, Py-H), 8.75 (s, 2H, PyH), 8.83 (s, 1H, Py-H).

2.8. Tetranuclear complex (3)

In a typical experiment, a solution of 7 mg K-oxone in 0.2 mL H_2O was added dropwise to a stirred solution of **2** (22 mg, 0.02 mmol) and $Mn(OAc)_2{\cdot}4H_2O$ (4.9 mg, 0.02 mmol) in 0.4 mL CH_3CN and 0.2 mL acetate buffer (0.05 M, pH 4.4). The reaction mixture was left under stirring for 15 min. Product **3** was then precipitated by addition of a saturated NH_4PF_6 solution. In NMR the Ru-bpy peaks were broadened and the terpyridine peaks including the $-CH_2-$ group had disappeared. EPR gave 16-line signal corresponding to ca. 5% Mn(III/IV) complex. Elemental analysis: found: C, 42.84; H, 3.21; N, 9.0; Mn, 4.95; calcd. for Mn(III/IV) complex: C, 42.00; H, 2.87; N, 9.07; Mn, 3.56. The tetranuclear complex could not be detected by ESI-MS.

An enriched sample was prepared in the same way as above except for the precipitation procedure. To the reaction mixture was added a saturated KNO_3 solution and the precipitate was filtered off to give 17.4 mg of crude complex. EPR gave 16-line signal corresponding to ca. 4% Mn(III/IV) complex. The strongly colored filtrate was precipitated with a saturated $NH_4\,PF_6$ solution to give 2.4 mg of complex with a relative concentration of Mn(III/IV) of ca. 40% according to EPR.

2.9. Trinuclear complex (8)

To a solution of 30 mg (0.24 mmol) of **2** in 1.6 mL of acetone was added 2.4 mg (0.12 mmol) $MnCI_2{\cdot}4H_2O$ in 0.8 mL H_2O. The resulting solution was stirred for 1 h, and the product was then precipitated by addition of NH_4PF_6 in H_2O, filtered and dried in a desiccator to give 28 mg. The product was analyzed without further purification. ESI-MS gave a doubly charged peak at *m/z* 1265 $[M - 2PF_6^-]^{2+}$, a triply charged peak at *m/z* 795 $[M - 3PF_6^-]^{3+}$ and a quadruply charged peak at *m/z* 560 $[M - 4PF_6^-]^{4+}$. NMR showed broad peaks for the Ru-bpy part and no, or very small broadened peaks for the terpyridine part of the compound. Elemental analysis: found: C, 46.11; H, 3.14; N, 9.83; calcd. C, 45.99; H, 3.00; N, 9.93.

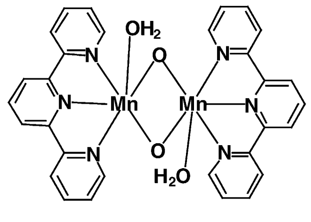
2.10. Trinuclear complex (9)

To a stirred solution of 50 mg (0.04 mmol) of **2**, in 10 mL MeOH was added 4 mg (0.02 mmol) $FeCl_2{\cdot}4H_2O$. The solution immediately turned dark due to the violet colour of the Fe-terpyridine complex. After stirring for 3 h, 2/3 of the solvent was evaporated, and the crude product was precipitated with NH_4PF_6, filtered and dried. The crude product was purified on a column of silica gel with $CH_3CN/H_2O/KNO_3$(sat. aq.) (90:7:3) as eluent. After evaporation of the solvent, the remaining solid was dissolved in acetone and precipitated by addition of a NH_4PF_6 solution, filtered and dried in a desiccator to give 50 mg of product **9**. Electrospray ionization mass spectrometry (ESI-MS) gave a doubly charged peak at *m/z* 1266 $[M - 2PF_6^-]^{2+}$, a triply charged peak at *m/z* 796 $[M - 3PF_6^-]^{3+}$ and a quadruply charged peak at *m/z* 561 $[M - 3PF_6^-]^{4+}$. Elemental analysis: found: C, 45.81; H, 3.19; N, 9.78; calcd.: C, 45.97; H, 3.00; N, 9.93.

3. Results and discussion

The intermediate ruthenium complex **2** was prepared as shown in Scheme 1. The methyl group of tolyl-terpyridine was brominated to give **4** and then reacted with phthalimide to give the protected amine **5**. After deprotection, the amine **6** was reacted with acid chloride **7**, giving the functionalized $Ru(bpy)_3$-complex **2**.

In the preparation of the dinuclear manganese complex **3**, the ruthenium-terpyridine complex **2** was first reacted with one equivalent of manganese(II) acetate, then the oxidant was added. Two different oxidants were used, K-oxone or $KMnO_4$ [28]. These oxidants have been used earlier in the preparation of $[(terpy)(H_2O)Mn^{III}(O)_2Mn^{IV}(OH_2)\text{-}(terpy)]_1^{3+}$. Product **3** was precipitated by addition of NH_4PF_6 or KNO_3. K-oxone gave the best results but it proved very difficult both to purify the product and to get reproducible results. From elemental analysis and spectroscopy, the crude complex **3** generally had a mixed dinuclear manganese(III, IV) and (IV, IV) core. The crude precipitate gave a distinguishable 16-line signal in EPR, see Fig. 1, indicating the formation of a manganese(III, IV) dimer, but results with several samples suggest that the relative amount of this component could be as low as 5%. In one experiment (see Section 2), which has been difficult to repeat, we managed to isolate a small amount of a complex, which gave an essentially clean 16-line EPR signal, characteristic of a dinuclear manganese(III, IV) (Fig. 2). This precipitate gave a much higher relative amount of complex **3**, but the overall yield was very low. The amount of sample was enough for EPR and photophysical studies discussed below. Due to the small amount of this sample the electrochemistry, MS and elemental analysis was performed on the crude precipitate with around 5% manganese(III, IV) dimer. In ESI-MS we found a peak corresponding to complex **2** but we did not find any peak corresponding to the dimer **3**. This might be



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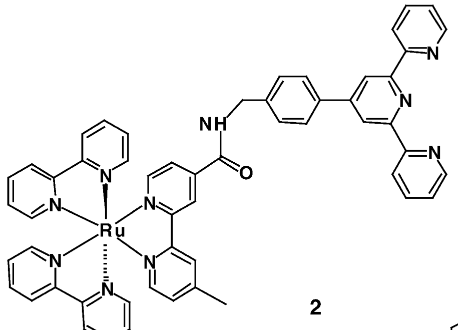

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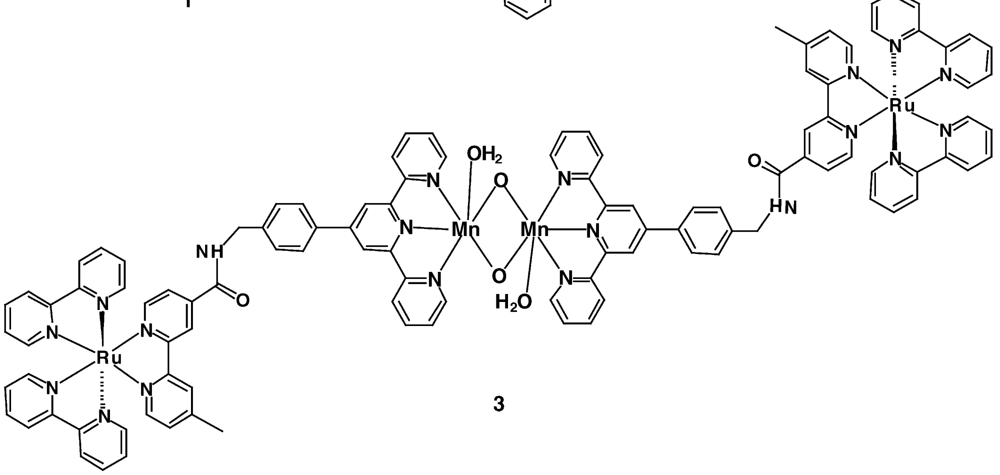
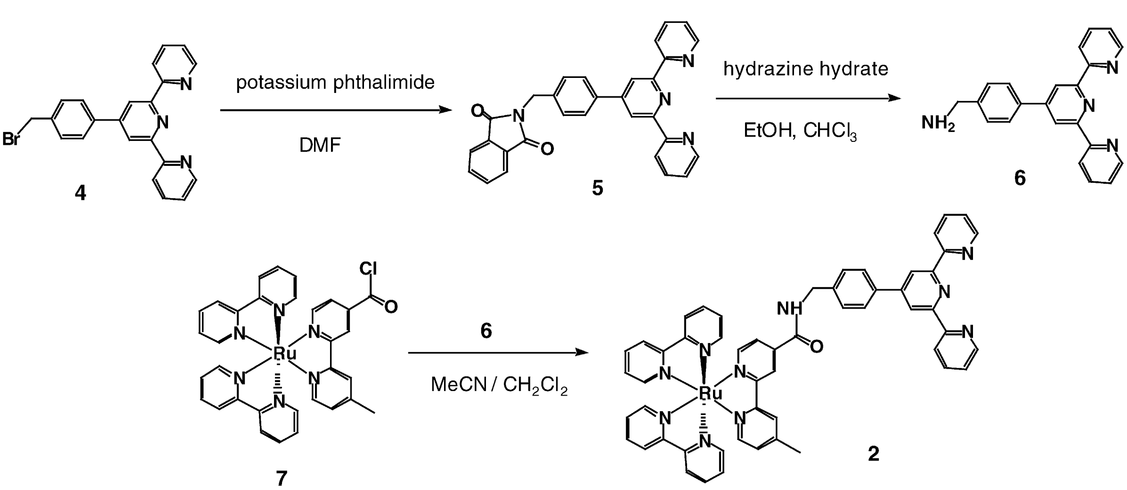


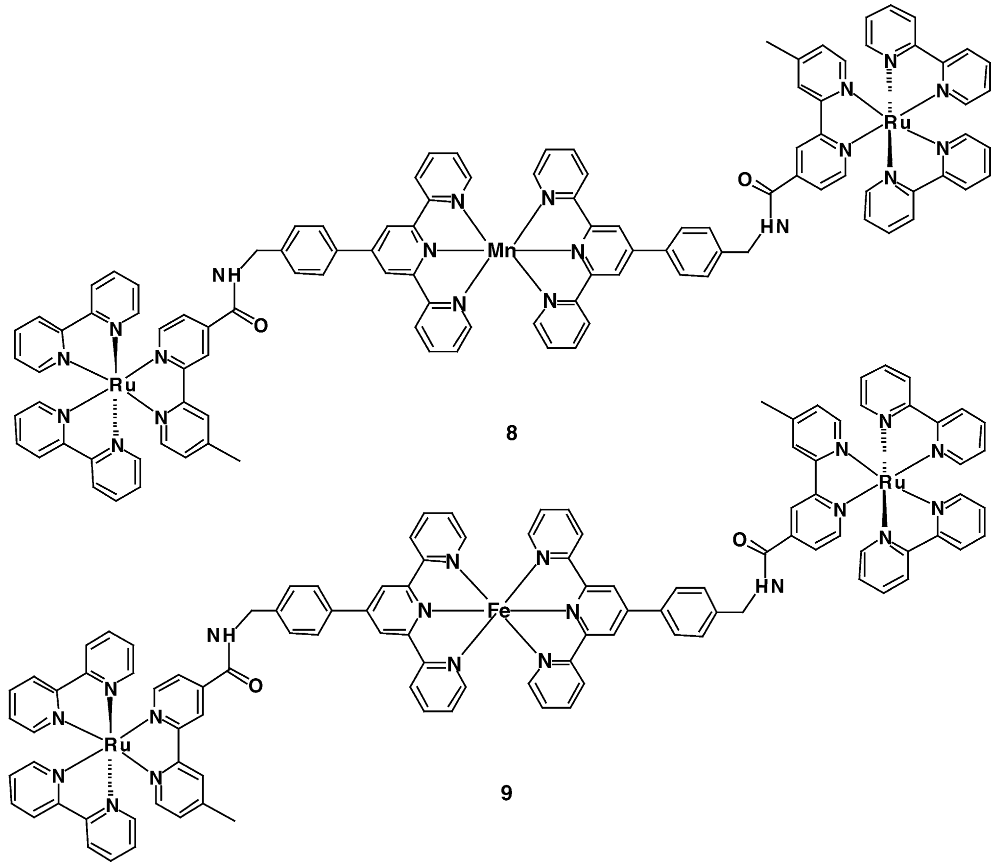
3

explained by the low concentration of dimer in the sample in combination with loss of manganese during the MS conditions, as also observed for the trinuclear complex **8**.

The reason why complex **3** is more difficult to prepare than the parent complex **1** is not clear. It could be an effect of the charge on the ruthenium(II) moiety on the redox properties of the complex. It could also be due to partial oxidation of ruthenium, since both oxone and permanganate are very strong oxidants. There could also be problems in the complexation between **2** and manganese, again because of the ruthenium moiety. In order to evaluate these factors, the preparation and properties of the complexes **8** and **9** was also studied. These complexes were readily formed by reacting the ligand complex **2** with the appropriate metal salt, **8** by reaction with manganese(II) chloride in acetone–water, **9** from the reaction with iron(II) chloride in methanol. Complex **9** was sufficiently stable to be purified by column chromatography while **8** very readily lost the coordinated manganese. Both complexes **8** and **9** could be characterized by elemental analysis and ESI-MS, but as in the case of **3**, extensive loss of manganese was observed with complex **8** in the MS.



Scheme 1. Synthetic procedure for complex **2**.



8

9

3.1. EPR spectroscopy

The enriched sample gave rise to a 16-line signal at $g \approx 2$ (Fig. 2) which is typical for a di-μ-oxo-bridged dinuclear manganese(III, IV) complex [29,30]. It can thus safely be attributed to the $Mn_2^{III,IV}$ core of complex **3**. By comparing with the parent dinuclear manganese(III, IV) complex **1**, we estimate that the sample contains ca. 40% of the manganese(III, IV) complex **3**. This estimate is supported by the photophysical studies, as shown below. By contrast,

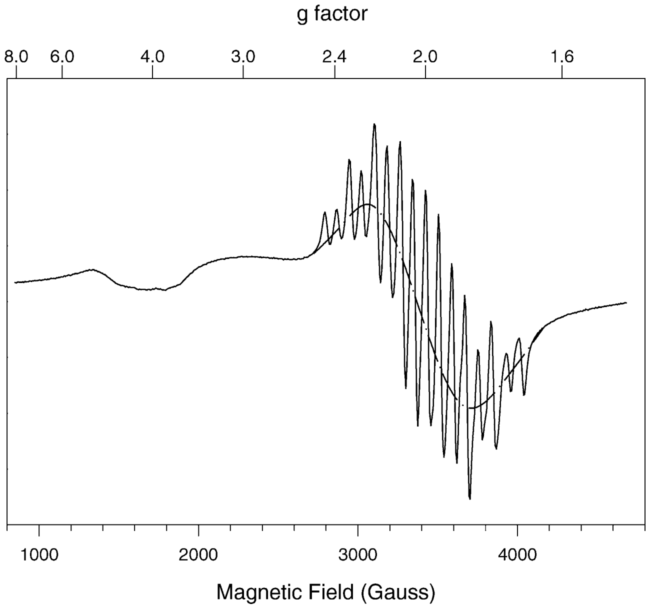


Fig. 1. EPR spectrum of **3**: 1 mg of **3** (crude product) dissolved in 200 μl acetonitrile. EPR conditions: resonance frequency, 9.59 GHz; microwave power, 20 mW; modulation amplitude, 10 G; temperature 6 K.

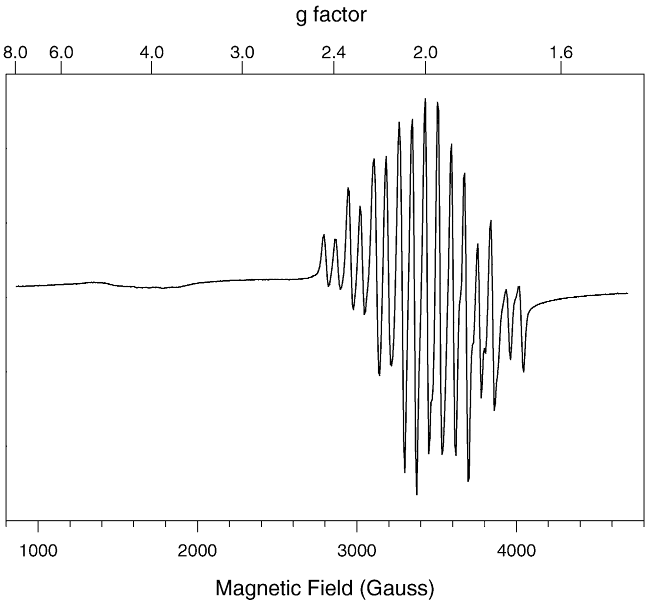


Fig. 2. EPR spectrum of 0.64 mM of **3** (purified, see text). EPR settings, see Fig. 1.

the crude samples contain only ca. 5% of this complex. A representative EPR spectrum of the crude samples is shown in Fig. 1. It appears to be a superposition of three different spectral features. In addition to the 16-line signal in the $g \approx 2$ region, there is a broad shoulder rising at ca. 1850 G and extending into the $g \approx 2$ region (dashed line in Fig. 1), and a weak, derivative shaped signal with crossover point at $g \approx 4.7$.

The nature of the broad, overlapping signal with double peaks in the $g \approx 2$ (wavy, partly dashed curve in Fig. 1) and $g \approx 3$ regions is not clear. However, it could be an indication of a dinuclear manganese(IV, IV) core since the shape of this signal is in qualitative agreement with the X-band EPR spectrum of an oxo-bridged manganese(IV, IV) complex, reported by Duboc-Toia et al. [31]. Accordingly we attribute this broad signal to a manganese(IV, IV) form of complex **3**. The formation of a manganese(IV, IV) core is consistent with the synthetic conditions, that is the use of very strong oxidants, either K-oxone or $KMnO_4$, in the preparation of complex **3**.

The weak signal in the $g \approx 4.7$ region, finally, probably originates from a monomeric Mn^{IV} moiety. Monomeric Mn^{IV} complexes are known to give signals around $g \approx 4$ as well as in $g = 2$ region at strong axial symmetry limits [32–41]. Since a manganese(II) complex **8** is readily formed, this is the most probable origin of a mononuclear Mn^{IV} which can give rise to an EPR signal at $g \approx 4.7$.

The synthesis of **3** thus gives a mixture of at least three products, the desired complex **3**, a related complex with a $Mn_2^{IV,IV}$ core and some monomeric Mn^{IV}-complex related to complex **8**.

3.2. Photophysics of 3

To further characterize complex **3**, its emission and absorption properties were studied in acetonitrile solution. The UV–vis absorption spectra of **2** and **3** were compared. In addition to the ruthenium-tris-bipyridine based transitions [42] the spectra of the manganese containing complex **3** showed an increased absorption around 340 nm. This absorption overlaps well with the one observed for the manganese(III, IV) dimer **1**. Upon irradiation of **3**, the 340 nm band was decreased.

Steady-state emission of **3** was compared with that of the manganese free complex **2**. Both complexes had an emission maximum around 635 nm. The emission intensity for **3**, though, was reduced to 40% of the intensity for complex **2**. In previous studies we have shown how similar manganese complexes efficiently can quench the triplet exited state of ruthenium [18,19]. If fast quenching of the exited state occurs in **3**, either through electron transfer or energy transfer, the emission results suggest that the sample consists of ~40% (**3**) and ~60% (**2**). Upon continuous irradiation of the samples, the emission intensity increased for **3** but stayed constant for **2**. It thus seems that the light sensitive complex **3** decomposes when it is exposed to light, perhaps by electron transfer from ruthenium to the high valent manganese, followed by dissociation of the reduced manganese ions.

Time resolved emission measurements showed that the enriched sample of **3** contained about 50% of a species with a long lived emission $\tau \sim 450$ ns, consistent with the emission lifetime of **2**, and 50% of a species with a very short lived emission, $\tau \sim 2$ ns, presumably **3**. This is in good agreement with the 40% $Mn_2^{III,IV}$ estimated from the EPR studies and measurements of steady-state emission.

3.3. Photophysical measurements of 8 and 9

The UV–vis absorption spectra of **8** and **9** both displayed increased absorption around 340 nm as compared to the non-metal ligated complex **2**. Complex **9** also showed an intense absorption around 570 nm ($\varepsilon \sim 10\,000$ M^{-1} cm^{-1}) from the Fe(terpy)$_2$ MLCT transition [43]. The coordination of manganese in **8** could not be detected by emission measurements, since no quenching was observed. The steady-state emission spectra showed the same emission intensity for **8** and the model complex **2** and the time resolved data only showed a single exponential $[Ru(bpy)_3]^{2+}$ based decay. It thus seems clear that complex **8** dissociates when it is dissolved in acetonitrile solution. However, when 10 equiv. of $MnCl_2$ salt were titrated into the sample, the emission was reduced to 75% of the initial value, suggesting that there is an equilibrium between coordinated and free manganese ions.

Since the iron(II) of complex **9** is much more strongly coordinated than manganese(II) and the quenching effect of the two ions should be of similar magnitude, complex **9** was also studied. It was found that the steady-state emission was strongly quenched to ~2% of the emission from **2**. This was in excellent agreement with time resolved measurements which showed that the sample contained 98% of a species with a short lived emission $\tau \sim 4.5$ ns and 2% of a species with a long lived emission, corresponding to **2**.

3.4. Electrochemistry

The redox potentials of complexes **3**, **8** and **9** were measured by cyclic voltammetry. Complexes **3** and **8** showed a reversible peak for Ru(II/III) at 0.99 V versus Ag/Ag^+, but neither the Mn(II/III) nor the Mn(III/IV) oxidation was seen. The reason for this is not clear, but we have earlier noticed problems with cyclic voltammetry of high valent manganese complexes coupled to ruthenium complexes. Another possible explanation is loss of coordinated manganese from the complexes **3** and **8** during the conditions for the electrochemical measurements.

By contrast, the voltammogram of complex **9** was unproblematic (Fig. 3) and showed two reversible oxidation peaks at 0.79 and 1.00 V. The peak at 0.79 V corresponds to the oxidation of Fe^{II}. It is slightly shifted to higher potential than for Fe(terpy)$_2^{2+}$ [44] due to the electron withdrawing

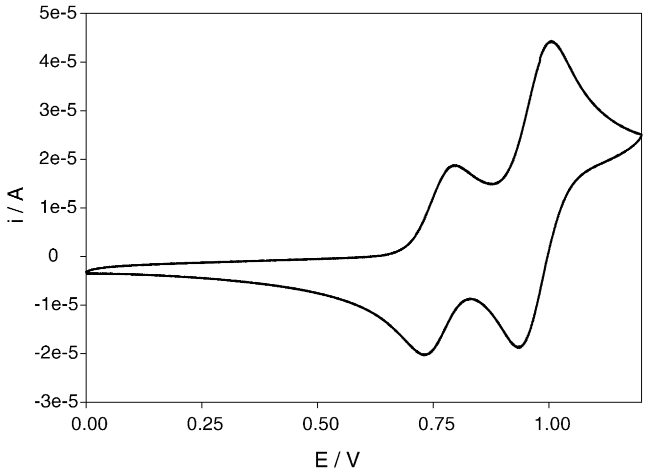


Fig. 3. Cyclic voltammogram of complex **9** (1.5 mM) in dry acetonitrile, with 0.1 M N-(n-C_4H_9)$_4PF_6$HH as electrolyte; scan rate: 0.1 V s^{-1}.

effect of the phenyl substituents. The second oxidation peak at 1.00 V corresponds to oxidation of Ru^{II}, and is similar to the one found for $Ru(bpy)_3^{2+}$.

3.5. Catalytic water oxidation

In order to study the catalytic properties of **3** for water oxidation, we prepared the complex in situ from complex **2** and manganese acetate. As a reference we also prepared complex **1**. On addition of oxone to a water solution of **1**, evolution of oxygen was observed, as described by Brudvig and coworkers [10]. Similar treatment of **3** gave oxygen evolution in a very similar fashion, see Fig. 4. However, also the addition of oxone to the manganese free complex **2** gave oxygen evolution, as might be expected from earlier studies of di- and terpyridine ruthenium complexes [45,46]. The curves for oxygen evolution were found to be different between complex **3** (curve (a) in Fig. 4) and complex **2** (curve (b) in Fig. 4). In case of complex **3**, where Mn ions were present in the water solution, the oxygen evolution was faster than that in the case of **2**. In both cases, the oxygen concentration reached ca. 150 μM at room temperature in ca. 8 min of addition after oxone. The clear difference in kinetics of oxygen evolution catalyzed by complexes **3** and **2** indicates different mechanisms for water oxidation.

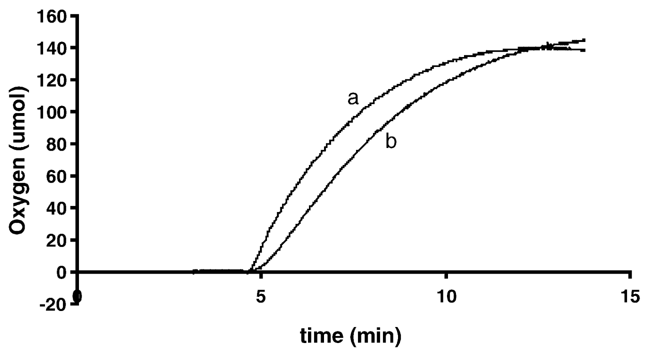


Fig. 4. Oxygen evolution in a 0.2 mM solution of complex **2** with 1 equiv. of MnOAc (a) or **2** without Mn (b) in 0.1 M acetate buffer (pH 4.4)/ acetonitrile (9:1); oxidant: K-oxone.

4. Conclusions

The tetranuclear Ru–Mn-complex **3** seems capable of oxidizing water chemically with oxone as oxidant, in analogy with the core complex **1** [11], but it does not appear to promote photochemical generation of oxygen. While this is disappointing, the facile synthesis of the ligand complex **2** seems very promising for the preparation of other types of complexes but **3**, where a redox active metal ion is linked to a $Ru(bpy)_3$-type of photosensitizer. This is nicely illustrated by the preparation of the trinuclear Ru-Fe complex **9**, which is stable, readily characterized, and photochemically well behaved.

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