

Intramolecular Electron Transfer from Mn or Ligand Phenolate to Photochemically Generated Ru^{III} in Multinuclear Ru/Mn Complexes. Laser Flash Photolysis and EPR Studies on Photosystem II Models

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Abstract: In a mononuclear Mn^{IV} and a trinuclear Mn^{II} complex, the ligands of which contain electron-rich phenols (coordinated to the Mn(‘s)) and covalently attached ruthenium(II) 2,2'-tris(bipyridyl)(=bpy)-type groups, intramolecular electron transfer (ET) from the phenolate ligand (in the mononuclear Mn^{IV} complex) or from a Mn^{II} (in the trinuclear Mn^{II} complex) to the photochemically ($\lambda_{\text{exc}} = 455 \text{ nm}$) generated Ru^{III} takes place with $k \geq 5 \times 10^7 \text{ s}^{-1}$, giving rise to the corresponding phenoxyl radical (complexed to Mn^{IV}) or to Mn^{III}, respectively. Thus, in the trinuclear Mn^{II} complex, the source of the electron that reduces the photogenerated Ru^{III}(bpy^{•-}) moiety is a Mn^{II}, in contrast to the situation with the mononuclear Mn^{IV} complex, where the electron stems from a phenolate. The half-life of the coordinated phenoxyl-type Ru(bpy)/Mn complex (as produced in the presence of [Co^{III}(NH₃)₅Cl]²⁺) is of the order 0.5–1 ms. The Ru(bpy) compound containing three (phenolate-ligated) Mn^{II} atoms is the first example of a photochemically induced intramolecular ET from a multinuclear Mn cluster to an attached “sensitizer”, and the Ru complex containing one (phenolate-ligated) Mn^{IV} is the first case of an ET from a synthetic Mn^{IV}-coordinated phenolate to a photochemically produced oxidant (Ru^{III}).

Introduction

In photosynthesis, water oxidation is accomplished by photosystem II (PSII), which is a large membrane-bound protein complex.^{1–4} To the central core proteins D1 and D2 are attached different cofactors, including a redox-active tyrosyl residue, tyrosine Z (Y_Z),^{1–5} which is associated with a tetranuclear manganese complex,⁶ these components constituting the so-called water oxidizing complex (WOC), the site in which the oxidation of water to molecular oxygen occurs.^{2,3,7}

On excitation of the primary electron donor chlorophylls, P₆₈₀, with a light quantum, an electron is transferred to the primary electron acceptor pheophytin, and subsequently to the quinones Q_A and Q_B.^{2,5} The oxidized P₆₈₀ has a reduction potential of 1.12 V/NHE and is reduced (=repaired) within nanoseconds by electron donation from Y_Z, which thereby is converted into a neutral radical, Y_Z[•].^{1,2,8,9} Y_Z[•] is reduced back^{1,10} by extraction of an electron from the Mn complex, which takes from 50 μs to 1.3 ms,¹¹ depending on the oxidation state of the Mn

complex.^{2–5,12–14} After four consecutive (light-driven) electron abstractions from the Mn cluster, which stores the accumulated oxidizing equivalents,^{15–18} oxidation of two water molecules takes place with the release of one oxygen molecule.

Concerning the function^{19–22} of the tyrosyl radical, which is located $\approx 5 \text{ \AA}$ away from the manganese cluster and 10–15 \AA from P₆₈₀,²³ it has been proposed that Y_Z[•] abstracts hydrogen atoms from water coordinated to the manganese cluster,^{11,24} in analogy with known metal–radical enzyme mechanisms²⁵ and in agreement with the results of quantum chemical calculations,²⁶

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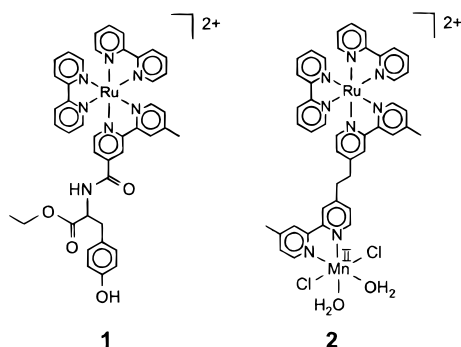
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which indicate that the O–H-bond strength in water coordinated to manganese complexes is lowered by about 30 kcal/mol, allowing direct hydrogen abstraction by a tyrosyl radical. This (new) concept involves the idea of the WOC being of metal-coordinated *radical* nature rather than a *metal* redox center.

With the aim of mimicking, on a basic level, the photoinduced electron transfer (ET) process from WOC to P_{680}^+ in the reaction center of PSII, ruthenium polypyridyl complexes have been used^{27–30} as photosensitizers, these compounds being particularly suitable since their photophysical and photochemical properties are very well known^{31–33} and since the reduction potential, $E(\text{Ru}^{\text{III}}(\text{bpy})_3/\text{Ru}^{\text{II}}(\text{bpy})_3) = 1.26 \text{ V/NHE}$ ^{34,35} (bpy = bipyridyl), is sufficiently positive to effect oxidation of phenols such as tyrosine ($E = 0.93 \text{ V/NHE}$).³⁶ As traps of the photochemically “mobilized” electron, viologens or a Co^{III} complex (as the respective chloride salts) were used.^{27–29} It was found that, when the $\text{Ru}^{\text{II}}\text{bpy}$ moiety connected to a phenol ligand (as with **1**) or complexed with a Mn^{II} (as with **2**) was excited in the presence of an external electron acceptor, intramolecular ET from the phenol or the Mn^{II} , respectively, to the photogenerated Ru^{III} took place.



After studying the formation and properties of metal complexes in which phenoxy radical is a ligand,^{37–40} we have now

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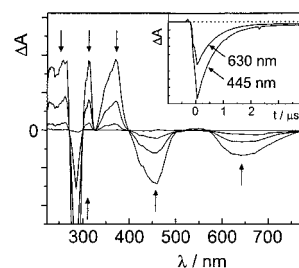


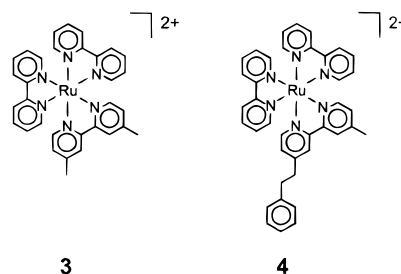
Figure 1. Spectra of transients measured 0.1, 0.3, 1, and 50 μs after 455-nm photolysis of a 70 μM solution of **4** in WAN 4:1. Inset: Decay of the (negative) signal at 630 nm due to fluorescence and the recovery of absorption at 445 nm.

synthesized⁴¹ a model system which contains a ruthenium tris-(bipyridyl)-type complex as photosensitizer covalently connected to phenolates, which in turn coordinate Mn ion(s), thus taking the modeling of PSII one step further. Here we report the results of photophysicochemical studies on two such systems (**8** (with one Mn^{IV}) and **9** (with three Mn^{II} 's)) and their building blocks.

Results and Discussion

All compounds described⁴² (in the following, {tbpy} represents a *generalized* tris-2,2'-bipyridyl unit, which includes ring-substituted ones; the *unsubstituted* 2,2'-bipyridyl moiety will be abbreviated as bpy) were dissolved in water–acetonitrile (\equiv WAN) mixtures 4:1 (v/v) and photolyzed with the 20-ns, 455-nm laser pulses ($\approx 5 \text{ mJ}$) from a Lambda Physik FL105M dye laser pumped with the 308-nm pulses from a Lambda-Physik EMG-MSC excimer laser. The 455-nm excitation light is close to the λ_{max} of the Ru{tbpy} metal-to-ligand charge transfer (MLCT) band. The time-resolved light-induced changes in the transmission of the solutions were detected spectrophotometrically and on-line converted into ΔA (absorption) values.^{37,43}

1. Tris-bpy-Type Ru Complexes Containing No Phenolate(s). The complexes synthesized⁴¹ and studied are shown below.



In Figure 1 are presented the time-dependent spectral changes ($\Delta A = f(t)$) observed on 455-nm photolysis (20-ns pulse) of a deoxygenated solution of compound **4** in WAN 4:1.

Clearly visible is the pulse-induced depletion of the 450-nm MLCT band and of the 290-nm ligand-centered (LC) transition of the parent, **4**. The *positive* ΔA 's at 310 and 370 nm are characteristic of the MLCT state of the ruthenium complex $[\text{Ru}^{\text{III}}(\text{bpy}^{\bullet-})]^{2+}$, formed by absorption of the 455-nm light, whereby the 370-nm band has been assigned to an LC transition of $\text{bpy}^{\bullet-}$.^{44,45} The *negative* signal ($-\Delta A$) at 600–700 nm (maximum at 620 nm) represents^{46–48} the light *emission*

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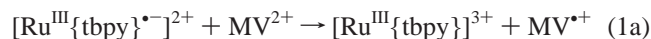
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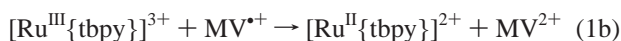
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resulting from the relaxation of $[\text{Ru}^{\text{III}}\{\text{tbpy}\}^{\bullet-}]^{2+}$ into the ground state, $[\text{Ru}^{\text{II}}\{\text{tbpy}\}]^{2+}$. As shown in the inset of Figure 1, this process is first-order, with $k = 1.8 \times 10^6 \text{ s}^{-1}$, which is exactly the same rate as that of the concomitant recovery of the 445-nm MLCT band and in excellent agreement with literature values^{47,49} for similar compounds in aqueous solution.

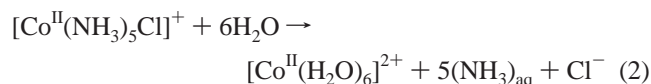
On addition of an electron scavenger such as methyl viologen (MV^{2+}) to solutions of **3** or **4** under photolysis, an electron transfer takes place from the MLCT state of **3** or **4** to MV^{2+} (eq 1a), with $k = (5-6) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (which is in very good



agreement with reference data⁴⁹⁻⁵¹), to yield $[\text{Ru}^{\text{III}}\{\text{tbpy}\}]^{3+}$ ($\lambda_{\text{max}} \approx 420 \text{ nm}$) and $\text{MV}^{\bullet+}$, with its characteristic absorption bands at 606 ($\epsilon = 13\,700 \text{ M}^{-1} \text{ cm}^{-1}$) and 396 nm ($\epsilon = 42\,100 \text{ M}^{-1} \text{ cm}^{-1}$).⁵² On a longer time scale, the electron transfer is reversible; i.e., Ru^{II} is regenerated (eq 1b), for which the rate constants measured ($7-8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) are again in excellent agreement with literature data for similar systems.^{29,53,54}

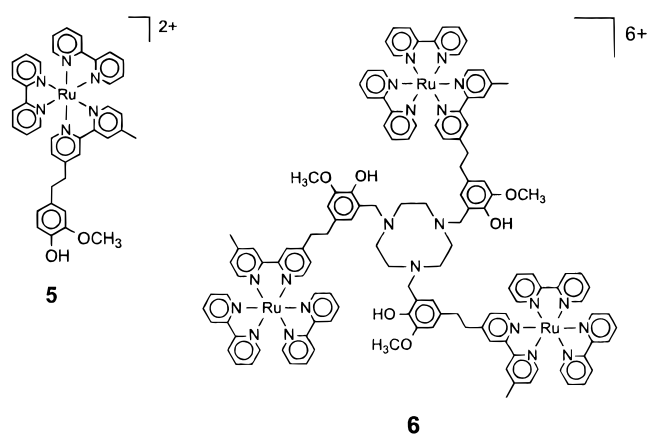


In the case of the oxidant $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$, the electron transfer from $[\text{Ru}^{\text{III}}\{\text{tbpy}\}^{\bullet-}]^{2+}$ ($k = 2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, in agreement with comparable cases⁵⁵) is irreversible due to hydrolysis of the Co^{II} complex thus formed:

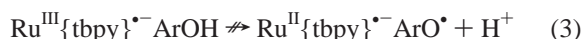


Thus, in the presence of $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$, $[\text{Ru}^{\text{III}}\{\text{tbpy}\}]^{3+}$ is the stable end product of the photolysis of **3** or **4**.

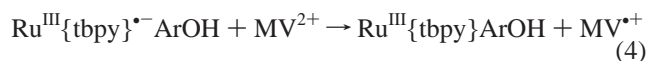
2. Phenol(ate)-Containing Ligands. 2.1. Laser Flash Photolysis (LFP) Results. In the phenol-containing compounds **5** (which is equivalent to **1**)²⁹ and **6** (a derivative of 1,4,7-triazacyclononane (tacn), which is a powerful ligand with respect to transition metals),^{41,56} the phenol moieties are expected (and have, in similar cases, already been observed²⁹) to participate in electron-transfer processes induced by photochemical production of Ru^{III} . On photolysis of these compounds in WAN 4:1 with the 455-nm light of the dye laser, emission at $\approx 620 \text{ nm}$ and transmission changes were observed of exactly the same type as described in section 1 for the systems containing *no* phenols. Thus, the conclusion from this is that the photochemically produced Ru^{III} in the $[\text{Ru}^{\text{III}}\{\text{tbpy}\}^{\bullet-}]$ moiety is *not* reduced by adjacent phenol groups; i.e., reaction 3 does *not* take place,



in analogy to results described for **1**.²⁷

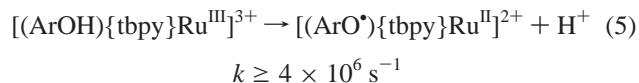


However, if the excess electron on the bpy ligand is removed by an external electron acceptor such as MV^{2+} or $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$,



$$k = (3-6) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

the resulting Ru^{III} , whose "vicinal electron density" is thus decreased compared to the case when the radical anion $\{\text{bpy}\}^{\bullet-}$ is the ligand, is reduced back to the Ru^{II} state (eq 5).⁵⁷



This is concluded from the observation that the absorption at $\approx 450 \text{ nm}$ (due to Ru^{II}), which decreased after the laser flash, increased again to exactly the level *before* the laser flash (i.e., quantitative regeneration of Ru^{II}), whereby the *rate* of regeneration (for **5**, $k = 9 \times 10^6 \text{ s}^{-1}$; for **6**, $k = 4 \times 10^6 \text{ s}^{-1}$) was the same as that for oxidation of the $\{\text{tbpy}\}^{\bullet-}$ moiety (eq 4), as monitored by the formation of $\text{MV}^{\bullet+}$ at 630 nm (see Figure 2). This means that the *intramolecular* electron transfer from the phenol to the $\text{Ru}^{\text{III}}\{\text{tbpy}\}$ moiety is faster than $(4-9) \times 10^6 \text{ s}^{-1}$; i.e., rate limiting under these conditions is the *bimolecular* reaction 4 and not the *unimolecular* reaction 5. Since the Brønsted acidity of phenol-type radical cations is ≥ 10 orders of magnitude higher than that of the parents,^{58,59} it is likely that the phenol group deprotonates upon electron transfer to Ru^{III} , as shown in eq 5 for compound **6**.

On a longer time scale, all the absorption changes induced by the laser pulse as monitored at 396 and 630 nm, the λ_{max} values of $\text{MV}^{\bullet+}$, disappear by second-order kinetics. Since there are no absorption changes at 445 nm (which means that the Ru^{II} concentration remains the same on this (long) time scale), the reaction is interpreted in terms of regeneration of the parent complex by reduction of the phenoxy-containing one-electron-

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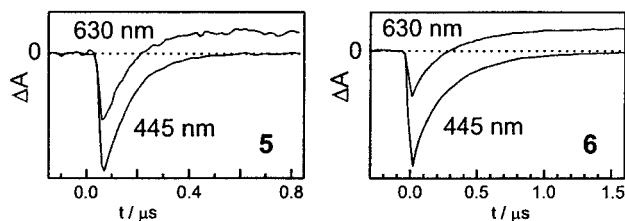


Figure 2. Absorption changes (ΔA) monitored at 630 (due to formation of MV^{+} , eq 4) and 445 nm (due to recovery of $Ru^{II}\{tbp\}$, eq 5) resulting from 455-nm photolysis of a 52 μM solution in WAN 4:1 of **5** or **6**, respectively, in the presence of 15 mM MV^{2+} .

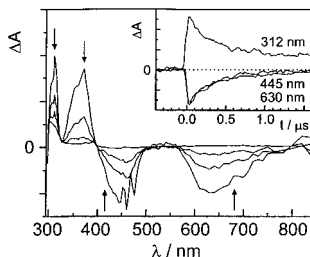
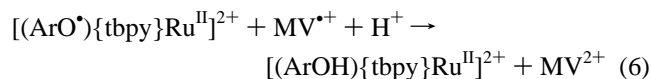


Figure 3. Spectra of transients recorded after 0.1, 0.3, 1, and 50 μs on photolyzing 52 μM **5** in the presence of 15 mM $[Co^{III}(NH_3)_5Cl]^{2+}$. Inset: Characteristic kinetic traces.

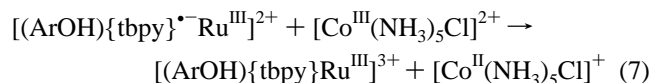
deficient complex by MV^{+} :



$$k = 1 \times 10^9 M^{-1} s^{-1} \text{ or } 2 \times 10^9 M^{-1} s^{-1} \text{ for } \mathbf{5} \text{ or } \mathbf{6}, \text{ respectively}$$

At $1 \times 10^9 M^{-1} s^{-1}$, the rate constant for this intermolecular “back electron transfer” is similar to the analogous one observed²⁹ in the case of **1**, and it is smaller than that ($(7-8) \times 10^9 M^{-1} s^{-1}$) measured for the corresponding back electron transfer to $[Ru^{III}\{tbp\}]^{3+}$ (see eq 1b). This is not unreasonable since, in the latter (eq 1b), the electron acceptor is (the stronger oxidant) Ru^{III} compared to ArO^{\bullet} in eq 6.

To support the formation of ArO^{\bullet} on electronic excitation of the Ru^{II} center, MV^{2+} was replaced by the “irreversible electron acceptor” $[Co^{III}(NH_3)_5Cl]^{2+}$, in analogy to the studies on **1**²⁹ and on **3** and **4** (section 1). Taking **5** as an example, the results are shown in Figure 3. Evident immediately after the pulse are the (negative signal of the) fluorescence at ≈ 630 nm, the depletion of Ru^{II} at ≈ 450 nm, and bands at 312 and 370 nm, due⁴⁵ to formation of $Ru^{III}\{tbp\}^{\bullet-}$. The rates of the “regeneration” processes as monitored at 312, 445, and 630 nm (see inset to Figure 3) increase with $[Co^{III}(NH_3)_5Cl]^{2+}$, and from this (linear) dependence (not shown), the rate constant obtained for both **5** and **6** according to



is $2 \times 10^8 M^{-1} s^{-1}$, a value equal to that measured for the case of the reference compounds **3** and **4** (see section 1). As can be seen in the inset of Figure 3, with **5** the absorption loss at 445 nm is quantitatively recovered relative to the situation before the laser pulse. This means that here the $Ru^{II}\{tbp\}$ unit is regenerated, which is in contrast to the situation for **3** or **4**, where the Ru^{III} complex is the (final) product (see section 1). The explanation is in terms of rapid intramolecular electron transfer

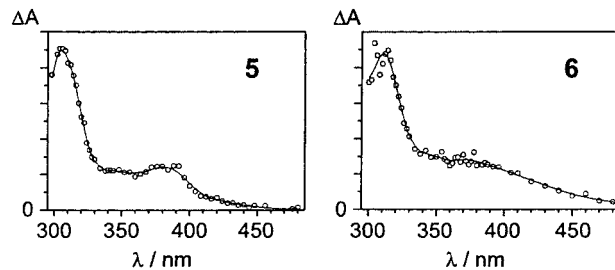


Figure 4. Spectrum measured 60 (for **5**) or 10 μs (for **6**) after flashing the solution described in Figure 3. The spectra are assigned to the phenoxyl-type radicals from **5** or **6**.

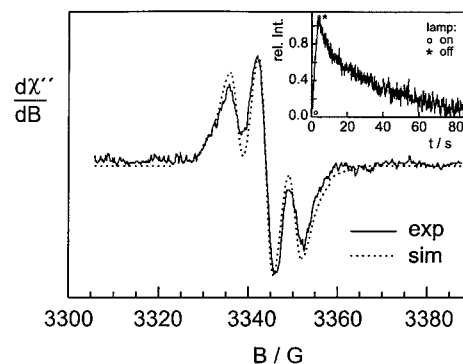


Figure 5. EPR spectrum recorded during photolysis of a solution in WAN 4:1 of 1.5 mM **6** in the presence of 10 mM $[Co^{III}(NH_3)_5Cl]^{2+}$ using a modulation amplitude of 4 G and 1 mW microwave power. The dotted line represents the spectrum simulated using the splittings indicated in Table 1.

from the $ArOH$ to the Ru^{III} moiety. Since the rate of this process could not be time-resolved, it must be $\geq 3 \times 10^6 s^{-1}$ ($=k_{\text{observed}}$ for oxidation of $Ru^{III}\{tbp\}^{\bullet-}$ by 15 mM $[Co(NH_3)_5Cl]^{2+}$, see above), which is in line with the number ($k \geq 9 \times 10^6 s^{-1}$) obtained in the experiment with MV^{2+} . The spectrum of the resulting phenoxyl-radical-containing complex is shown in magnified version in Figure 4. The spectrum with the bands at 306 and 380 nm is similar to those of 2-MeO-phenoxyl⁶⁰ and of 2,6-di-*tert*-butyl-4-methoxyphenoxyl radical,⁶¹ and the extinction coefficients⁶² in the range $(0.3-1) \times 10^4 M^{-1} cm^{-1}$ are also similar.

2.2. EPR Detection. Solutions of the same compositions as those described in the LFP experiments were subjected to continuous (“in situ”) photolysis in the EPR cavity of a modified⁶³ Varian E9 spectrometer using the focused and filtered light ($\lambda \geq 395$ nm) of a xenon lamp while the EPR spectrum was recorded. In the case of the “non-phenolic” reference compounds **3** and **4**, absolutely no EPR signals were detected. In contrast, with the phenol(ate)-containing compounds, relatively strong 1:2:1 triplet signals were seen. As an example, in Figure 5 is presented the spectrum recorded on in situ photolysis of a solution containing **6**.

The 1:2:1 signal from **6** with a splitting of 6.2 G and $g = 2.0046$ disappears with a half-life of ≈ 20 s when the light is turned off. In the case of **5**, after the exciting light focused into the EPR cavity was turned off, the triplet signal decayed,

(60) O'Neill, P.; Steenken, S. *Ber. Bunsen-Ges. Phys. Chem.* **1977**, *81*, 550.

(61) Sokolowski, A. Ph.D. Dissertation, Ruhr-Universität, Bochum, Germany, 1996.

(62) Estimated from the measured pulse-induced absorption changes at 450 nm in comparison with those for the reference compound **1** and assuming a quantitative electron transfer from $ArOH$ to Ru^{III} , see: Burdinski, D. Ph.D. Dissertation, Ruhr-Universität, Bochum, Germany, 1998.

(63) See: Hildenbrand, K. *J. Chem. Soc., Perkin Trans.* **1995**, 2153.

Table 1. EPR Parameters of Phenoxy-Type Radicals in Solution

parent phenol	phenoxy radical	splitting (G) due to methyl(ene) H's	ring protons	<i>g</i>	ref(s)
4-methylphenol	4-methylphenoxy	12 (para)	6.0 (ortho)		65
2,4-dimethylphenol	2,4-dimethylphenoxy	6.5 (ortho)	6.5 (ortho)		66
		11.2 (para)			
2,6-dimethyl-4-ethylphenol	2,6-dimethyl-4-ethylphenoxy	6.0 (ortho)			65
		9.1 (para)			
2-methoxyphenol	2-methoxyphenoxy	1.8 (<i>o</i> -OCH ₃)	~4.3 (ortho) ~8.5 (para)	2.00439	48, 65, 67
4-allyl-2-methoxyphenol	4-allyl-2-methoxyphenoxy	8.0 (<i>p</i> -CH ₂)	4.1 (ortho)		68
		1.6 (<i>o</i> -OCH ₃)			
4-carboxymethyl-2-methoxyphenol	4-carboxymethyl-2-methoxyphenoxy	7.1 (<i>p</i> -CH ₂)	6.1 (ortho)	2.0043	69
		1.3 (<i>o</i> -OCH ₃)			
5	<i>a</i>	6.0 (para)	<i>b</i>	2.0044	<i>c</i>
6	<i>a</i>	6.3 (para)	<i>b</i>	2.0046	<i>c</i>

^a See text. ^b The splittings due to ortho or meta ring protons are \leq the line width. ^c This work.

independent of field position, with the shorter half-life of ≈ 1 s, which decreased on increasing the exciting light intensity, indicating contributions of second-order decay kinetics.

As mentioned, in the case of **6**, the half-life is ≈ 20 s. In **6**, a molecule containing *three* phenolate ligands connected to the central tacn ring, several intramolecular H-bonds are possible which probably protect the phenoxy radical from rapid intermolecular (radical–radical) decay.^{38,64}

In Table 1 are collected the EPR parameters of the phenoxy-type radicals obtained from **5** and **6**, together with those of model phenoxy radicals from the literature.

It is evident from the splittings of the methylene group ($a_{\text{para}} \approx 6$ G) that the distribution of spin in the phenoxy radical is similar to that in “simple” phenoxy radicals.⁷⁰ Also, the *g*-factors of the “complex” phenoxy radicals are comparable with those (≈ 2.004)^{65,71,72} of the “simple” ones. In this connection, it is interesting that the *g*-factor of the tyrosine Z radical of the WOC has the similar value, 2.0045.⁷³

3. Mn Complexes 7 and 8. In compound **7**, *three* phenolate ligands, connected by a tacn ring, are coordinated to the central Mn^{IV}. The compound can be reversibly oxidized electrochemically ($E = 0.56$ V vs Fc^{+/0}).⁷⁴ The one-electron-oxidized form was characterized spectroscopically to consist of a phenoxy radical coordinated to the Mn^{IV} ion.^{38,61} The corresponding complex (having, however, the MeO group in the ortho position) containing [Ru^{II}{tbpv}] units is **8**. Unfortunately, its *electrochemical* oxidation, by which the coordinated phenoxy radical is expected to be formed, turned out to be *irreversible*, although

(64) In the WOC, upon oxidation of Y_Z, the phenolic proton is transferred to an adjacent histidine via a preexisting intramolecular H-bond (see: Hays, A.-M. A.; et al. *Biochemistry* **1998**, *37*, 11352. Diner, B. A.; et al. *Biochemistry* **1998**, *37*, 17931. Mamedov, F.; et al. *Biochemistry* **1998**, *37*, 14245. O'Malley, P. J. *J. Am. Chem. Soc.* **1998**, *120*, 11732).

(65) Stone, T. J.; Waters, W. A. *J. Chem. Soc.* **1964**, 213.

(66) Huysmans, W. G. B.; Waters, W. A. *J. Chem. Soc. (B)* **1966**, 1047.

(67) Dixon, W. T.; Moghimi, M.; Murphy, D. J. *Chem. Soc., Faraday Trans. 2* **1974**, 1713.

(68) Thompson, D.; Norbeck, K.; Olsson, L. I.; Constantin-Teodosiu, D.; Van der Zee, J.; Moldeus, P. J. *Biol. Chem.* **1989**, *264*, 1016.

(69) Valavanidis, A.; Gilbert, B. C.; Whitewood, A. C. *Chim. Chron., New Ser.* **1995**, *24*, 217.

(70) The smaller ring splittings seen for the “simple” phenoxy radicals are buried in the large line-width characteristic of the “complex” (= intermediate molecular weight) phenoxy radicals. As is evident from Table 1, the methoxy substituent decreases the spin density such that the splittings at the ortho and para positions are decreased.

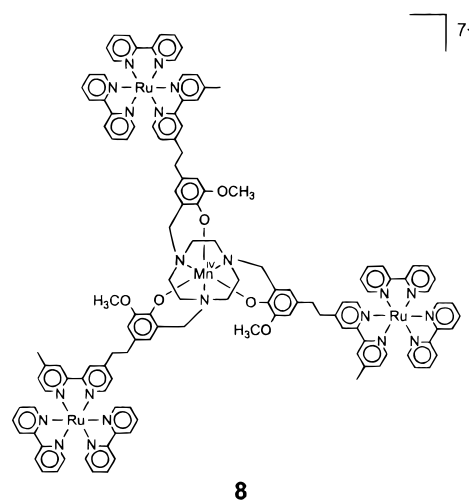
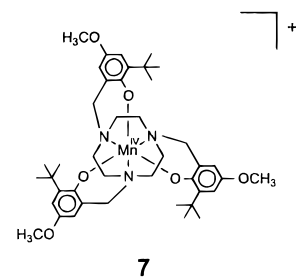
(71) Davies, A. G.; Howard, J. A.; Lehnig, M.; Roberts, B. P.; Stegmann, H. B.; Uber, W.; In *Landolt-Börnstein*; Fischer, H., Hellwege, K.-H., Eds.; Springer: Berlin, 1979; Vol. 9c, p 2.

(72) Barry, B. A.; Babcock, G. T. *Chem. Scr.* **1988**, *28A*, 117.

(73) Babcock, G. T.; Sauer, K. *Biochim. Biophys. Acta* **1975**, *376*, 315.

(74) All potentials refer to the Fc^{+/0} couple in acetonitrile, unless specified otherwise.

a potential of ≈ 0.85 V can be estimated.⁴¹ The obvious question is whether the oxidized species can be produced alternatively, e.g., by *photochemical excitation* of the Ru^{II}{tbpv} moiety.



In Figure 6 is shown the spectrum observed on 445-nm photolysis of a 20 μ M solution of **8** in WAN 4:1.

From inspection of the figure, it is obvious that even in the short time of 200 ns after the 20-ns pulse, there is no fluorescence visible; thus, the MLCT state is quenched in ≤ 200 ns.⁷⁵ This interpretation is supported by the fact that the absorption at 445 nm, the MLCT band of Ru^{II}{tbpv}, returns to the prepulse level in a similarly short time. These observations indicate the occurrence of a fast intramolecular electron transfer,⁷⁶ which can, in principle, proceed by eq 8a or b, these processes differing by the nature of the intramolecular electron

(75) Note the *long* lifetime of the MLCT state in the model compound **1**.

(76) Quenching by energy transfer (Hammarström, L.; et al. *Biochim. Biophys. Acta* **1998**, *1365*, 193) can be excluded on the basis of the observations described below.

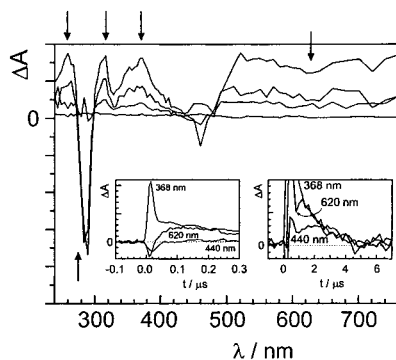
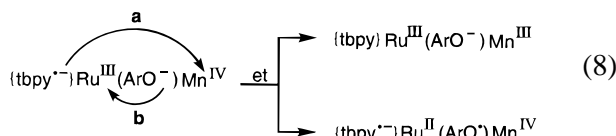


Figure 6. Spectra recorded 0.05, 0.2, 2, and 20 μs after flashing a 20 μM solution of **8** in WAN 4:1. Insets: Kinetic traces at the indicated wavelengths.

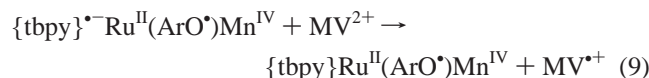
donor and acceptor:



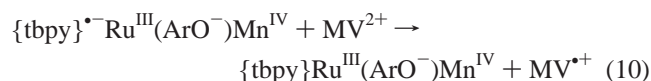
The following arguments serve to differentiate between paths a and b in eq 8. The positive ΔA 's at $\lambda \geq 500$ nm can be explained only in terms of production of the $\text{Ru}^{\text{II}}\{\text{tbpy}\}^{\bullet-}$ unit (ϵ values $(1-1.5) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).⁷⁷⁻⁸⁰ In line with this are the positive ΔA 's at ≈ 350 nm, where the Ru^{II} -coordinated $\text{bpy}^{\bullet-}$ moiety also absorbs ($\epsilon_{350} \approx (1-2) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$),⁷⁷⁻⁸⁰ all this supporting path b. In addition, the alternative, path a, can be discarded on the basis of the fact that the $\text{Ru}^{\text{III}}\text{Mn}^{\text{III}}$ unit that would result from reaction a does not absorb at $\lambda \geq 450$ nm, the MLCT absorption band of the $\text{Ru}^{\text{II}}\{\text{tbpy}\}$ unit.⁵³ Thus, if path a were right, at 445 nm, the initial light-induced depletion would persist; i.e., at this wavelength there would be *no recovery* to the prepulse level, which is in contrast to observation (Figure 6).

As can be seen in the insets of Figure 6, the "repair" of $\{\text{tbpy}^{\bullet-}\}\text{Ru}^{\text{II}}$ to yield $\{\text{tbpy}\}\text{Ru}^{\text{II}}$ consists kinetically of two components, the first (the major one) occurring on the ≈ 100 -ns time scale and the second within several microseconds. At present, we have no explanation for this phenomenon.

Also, in the presence of MV^{2+} , the decay of the MLCT state is very fast, giving rise to long-lived absorptions at 396 and ≥ 600 nm. These are due to MV^{2+} .⁵² This proves that an electron transfer has occurred. Concomitant with the formation of $\text{MV}^{\bullet+}$, the absorption at 440 nm, which is due to the $\text{Ru}^{\text{II}}\{\text{tbpy}\}$ moiety, returns to the prepulse level. These observations are explained in terms of eq 8b, followed by eq 9.



Rather than $\{\text{tbpy}\}^{\bullet-}\text{Ru}^{\text{III}}(\text{ArO}^-)\text{Mn}^{\text{IV}}$ undergoing the *intramolecular* ET according to eq 8b, followed by the *intermolecular* ET via 9, at sufficiently high concentration of MV^{2+} the order may be reversed, i.e., *intermolecular* ET to MV^{2+} ,



(77) Anderson, C. P.; Salmon, D. J.; Meyer, T. J.; Young, R. C. *J. Am. Chem. Soc.* **1977**, *99*, 1980.

(78) Mulazzani, Q. G.; Emmi, S.; Fucchi, P. G.; Hoffman, M. Z.; Venturi, M. *J. Am. Chem. Soc.* **1978**, *100*, 981.

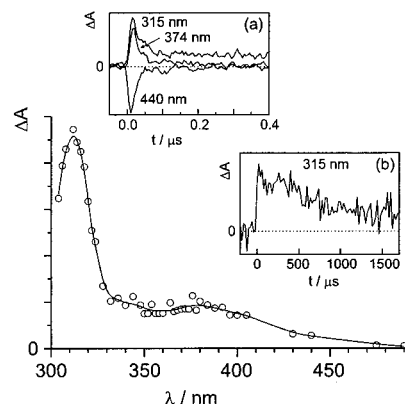
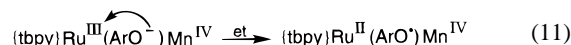


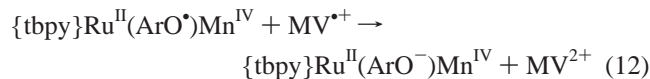
Figure 7. Absorption spectrum measured 10 μs after flashing a 23 μM solution of **8** in the presence of 15 mM $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$.

followed by the *intramolecular* ET,



At present, no attempt was made to differentiate between these alternatives.⁸¹

The oxidation of $\{\text{tbpy}\}\text{Ru}(\text{ArO})\text{Mn}^{\text{IV}}$ according to eq 9 or 10 is reversible; i.e., the photooxidized complex which contains ArO^* is back-reduced:

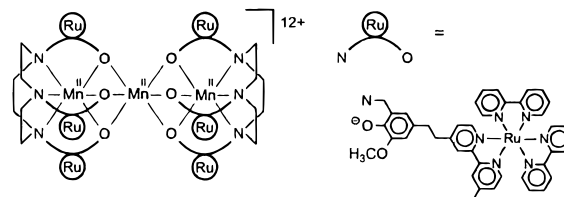


The rate constant for this process, as measured from the absorption change at 610 nm, is of the order $10^9-10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

An analogous experiment was performed using $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ as oxidant in place of MV^{2+} . In <50 ns after the laser flash, the concentration of the $\text{Ru}^{\text{II}}\{\text{tbpy}\}$ moiety was back to its prepulse level, as monitored at 370 and 450 nm (see Figure 7, inset a).

The spectrum recorded at the time (10 μs) after completion of the reactions described above is shown in Figure 7. This spectrum with bands at 310–315 and 380 nm is similar to those of (the uncomplexed) phenoxyls shown in Figure 4. It decays slowly within 1–2 ms (see inset b in Figure 7). On this basis, it is identified in terms of a phenoxyl radical which is suggested to be coordinated to the central Mn^{IV} . The strongly reduced lifetime as compared to that of the *uncoordinated* complex (1–20 s, see above) is ascribed to the decreased electron density of the phenoxyl moiety due to coordination to the Lewis-acidic Mn^{IV} .

4. Complex 9. **9** was photolyzed the same way and under the same conditions as described in the preceding. After



9

excitation, the only transient seen was the MLCT state, which decayed with $\approx 5 \times 10^7 \text{ s}^{-1}$, as concluded from the rapid

(79) Heath, G. A.; Yellowlees, L. J.; Brateman, P. S. *J. Chem. Soc., Chem. Commun.* **1981**, 287.

(80) Bugnon, P.; Hester, R. E. *Chem. Phys. Lett.* **1983**, *102*, 537.

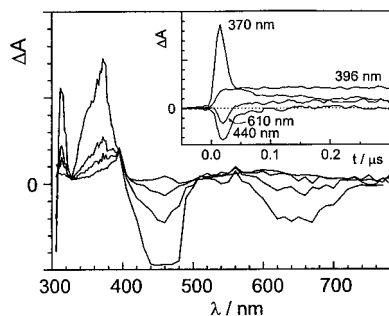
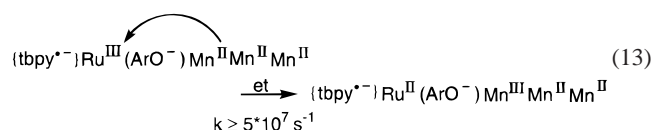


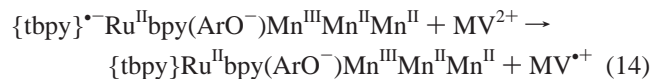
Figure 8. Spectra of transients from the 455-nm photolysis (20 ns) of 12 μM **9** in the presence of 15 mM MV^{2+} measured 0.02, 0.04, 0.06, and 2 μs after the pulse.

decrease of the fluorescence at 620 nm and the absorption recovery at 450 nm. Since there was no spectroscopic evidence at any wavelength and any time (>20 ns) for the formation of a phenoxyl-type species, the Mn^{II} cluster must be the ultimate intramolecular electron source (see eq 13). This is in accord



with the lower first oxidation potential of the Mn^{II} cluster (≈ -0.4 V vs Fc^+/Fc) compared to that of a phenolate moiety, which is anticipated to be $\approx +0.8$ V (see corresponding potentials of **5** (+0.77 V) and **8** (+0.85 V)).⁴¹

The product of the process described in eq 13, i.e., the moiety $\{\text{tbpy}^{\bullet-}\text{Ru}^{\text{III}}\}$, can again be scavenged by oxidants such as MV^{2+} or $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$. The resulting situation is shown in Figure 8. Visible are the fast decay of the fluorescence at ≥ 600 nm, the equally rapid decay of the characteristic absorption at 370 nm of the MLCT state, and the recovery of the absorption at 440 nm of the Ru^{II} MLCT transition.⁸² The corresponding formation of MV^{+} is seen at 396 and 610 nm. The observations are explained in terms of reaction 13 followed by reaction 14. The spectroscopic consequences of the change of oxidation



state from Mn^{II} to Mn^{III} are expected to be small and uncharacteristic.⁸³ In line with this expectation, no further spectroscopic changes were observed as reaction 14 proceeded.

Summary and Conclusions

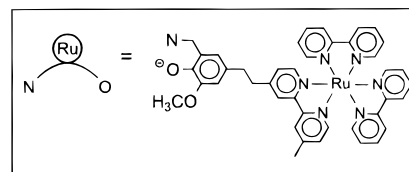
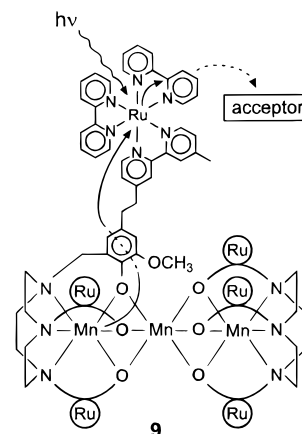
It has been found that 455-nm photolysis of $\text{Ru}^{\text{II}}\{\text{tbpy}\}$ -type complexes in the presence of external electron scavengers such as MV^{2+} or $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ leads to the production of the strongly oxidizing $\text{Ru}^{\text{III}}\{\text{tbpy}\}$ moiety, in agreement with earlier studies.²⁹ In $\text{Ru}-\text{Mn}^{\text{IV}}$ complexes with bpy-type ligands functionalized with electron-rich phenols (as in **8**), intramolecular electron transfer to Ru^{III} from the phenolate ligand takes place with $k \geq 5 \times 10^7 \text{ s}^{-1}$, giving rise to the corresponding (complexed) phenoxyl radical. This rate constant is ≥ 3 orders of magnitude higher than that ($5 \times 10^4 \text{ s}^{-1}$) for the similar complex **1** studied²⁹ previously. The reasons for this difference are possibly (a) the higher electron-donating power of the

(81) This would be possible by a variation of the concentration of MV^{2+} . However, we are planning to measure the rate of eq 8b or 11 *directly* using a time resolution better than the presently available 20 ns.

(82) As in the case of **8**, there seem to be two kinetic components in these processes; see inset to Figure 8.

(83) See: Burdinski, D. Ph.D. Dissertation, Ruhr-Universität, Bochum, Germany, 1998.

Scheme 1



(methoxylated) phenol as compared to the situation in **1** and (b) the shorter length of the “spacer” between the phenol and Ru^{III} .⁷⁵

In the trinuclear Mn^{II} complex **9**, the source of the electron that reduces the photochemically generated $\text{Ru}^{\text{III}}\{\text{tbpy}\}^{\bullet-}$ moiety is not a phenolate but a Mn^{II} . The ET situation may be visualized as in Scheme 1, whereby the electron transfer from Mn^{II} to Ru^{III} may or may not proceed through the connecting phenolate moiety. To check on this, a time resolution better than 20 ns would be necessary.

In this complex, with respect to Ru^{III} , Mn^{II} is apparently a better reductant than phenolate. In contrast, in the Mn^{IV} complex **8**, the electron is extracted from a phenolate. This is not surprising since in this case the Mn is in a higher oxidation state. A further point of interest is the large difference in lifetime between the phenoxyl radical from **1** and those described in *this* work: Whereas in the case of **1** the half-life of the phenoxyl radical (as produced in the presence of $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$) is 50 ms, it is $\geq 1 \text{ s}^{-1}$ for those from **5** and **6**. This difference is probably related to the larger electron density⁸⁴ (due to the electron-donating OCH_3 substituent) and, in addition, to the steric inaccessibility of the phenoxyl radical which is hidden in the H-bonding network,⁸⁵ thus preventing a rapid radical–radical decay in the latter case.⁸⁶

The compound **9** ($\text{Mn}^{\text{II}}\text{Mn}^{\text{II}}\text{Mn}^{\text{II}}$) is the first example of a photochemically induced intramolecular electron transfer from a *multinuclear* Mn cluster to a covalently attached “sensitizer”, and the complex **8** is the first example of an electron transfer from a Mn^{IV} -coordinated phenolate to a photochemically produced oxidant (Ru^{III}). It is hoped that the understanding of the photochemistry of these complexes will be helpful in elucidating the mechanism(s) by which the water oxidizing complex operates.

Acknowledgment. We are grateful to Marion Toubartz for her highly qualified help with the LFP experiments and to Dr. K. Hildenbrand for performing and analyzing the EPR measurements.

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(84) The influence of electron density can be seen from the much shorter half-life of the Mn^{IV} -coordinated radical as compared to that of the “free” one.

(85) As concluded from crystal data on similar compounds; see ref 38.

(86) Nature may have developed an analogous strategy to prevent undesired side reactions of Y_2^* in the WOC.