



Review Polynuclear Cobalt Complexes as Catalysts for Light-Driven Water Oxidation: A Review of Recent Advances

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Abstract: Photochemical water oxidation, as a half-reaction of water splitting, represents a great challenge towards the construction of artificial photosynthetic systems. Complexes of first-row transition metals have attracted great attention in the last decade due to their pronounced catalytic efficiency in water oxidation, comparable to that exhibited by classical platinum-group metal complexes. Cobalt, being an abundant and relatively cheap metal, has rich coordination chemistry allowing construction of a wide range of polynuclear architectures for the catalytic purposes. This review covers recent advances in application of cobalt complexes as (pre)catalysts for water oxidation in the model catalytic system comprising [Ru(bpy)₃]²⁺ as a photosensitizer and S₂O₈²⁻ as a sacrificial electron acceptor. The catalytic parameters are summarized and discussed in view of the structures of the catalysts. Special attention is paid to the degradation of molecular catalysts under catalytic conditions and the experimental methods and techniques used to control their degradation as well as the leaching of cobalt ions.

Keywords: polynuclear cobalt complexes; water oxidation; artificial photosynthesis

1. Introduction

Currently, worldwide energy demand is satisfied mostly with fossil fuels, such as gas, oil, and coal [1,2]. Although these energy resources are rather easy to use, they contain a few principal drawbacks: limited stock, high consumption of O₂ as well as high CO₂ emission and, finally, high risk of environmental pollution. It is for these reasons that the search for highly efficient energy sources has been of high interest during the last decades. The use of sunlight, as an inexhaustible energy source with the ground level flux of ca. 1360 W m⁻² [3], is an attractive alternative to fossil fuels. The chemical approach to sunlight energy utilization is to develop photo-driven processes able to replace the existing environmentally non-friendly ones. The photosynthesis of carbohydrates from CO_2 and water, occurring in natural biosystems, represents a perfect model to be studied [4]. The energy for this process is provided by photosystem (PSI and PSII) protein complexes, and through the formation of ATP and NADPH under visible light exposure. In brief, (for recent reviews see [5-10]), upon irradiation, the photosensitizer (chlorophyll) in the PSII abstracts electrons from a water-oxidizing complex (WOC). The latter oxidizes water and releases O_2 to close the catalytic cycle within the PSII system. The four-electron process of water oxidation, which also produces four protons, consumes significant energy and, at the same time, is potentially attractive for practical applications when protons are reduced to H_2 [10–12].

While the existence of biological photosynthesis has been known for a long time [13], the principal details about the structure of the PSII and WOC were obtained only in 21st century [14,15]. The first

single crystal X-ray structure analysis of the catalytically active PSII from cyanobacterium at 3.8 Å resolution was accomplished in 2001, but the structure of the WOC was not resolved in detail [16]. Just few years later (in 2004 and 2005) a better set of data, collected at 3.5 and 3.0 Å resolutions, allowed researchers to propose a cubane-like Mn_3CaO_4 structure of the WOC [17,18]. In 2011 the experimental results were improved by collecting the data at 1.9 Å [19], revealing that the structure of the WOC contains four manganese atoms, where cubane fragment Mn_3CaO_4 is accompanied with the fourth Mn atom bridged to cubane with two oxygen atoms (Figure 1). The oxygen-evolving mechanism presumes stepwise oxidation of manganese atoms to Mn^{IV} and/or Mn^V with formation of high-valent metal-oxo species, which oxygen atoms "join" to release O₂ molecules [5,20-22]. The role of redox-inactive calcium is still not fully clear [5,23]. Most probably, the calcium center acts as a Lewis acid and coordinates water molecules, thus assisting the mechanism [23,24]. Calcium could influence the redox potentials of the manganese cluster, as evidenced by the model studies [25–27]. Also, it was demonstrated that Ca²⁺ is required for the assembly of the oxygen-evolving center (OEC) [23,28]. The mechanism of action of the PSII has been the subject of numerous experimental and theoretical investigations (which are far from the final conclusion) and we would like to refer readers to the recent reviews on this topic [5,6,8,9,15].



Figure 1. Overall structure (left) and Mn₄CaO₄ site (right) in PSII (PDB code 3WU2). Colour scheme: Mn, violet; Ca, grey; O, red; N, blue; C, grey (small balls). M–O–M bonds are highlighted by yellow.

From the point of view of coordination chemistry, the complex bearing Mn₃CaO₄ or Mn₄CaO₄ core looks relatively simple. Cubane, $M_4(\mu_3-O)_4$, is the most widespread molecular structure type for tetranuclear coordination compounds [29] with more than 1000 examples in the Cambridge Structural Database (CSD) [30]. Discovery of the WOC structure of the PSII, inspired chemists to synthesize model coordination compounds having related polynuclear assemblies (biomimetic approach) and redox potentials [25–27]. The principal idea of this approach was to design well-defined molecular systems that allow for the studying of the mechanisms of action. An artificial water oxidation system comprises the same principal components as the natural one: photosensitizer, catalyst, and electron acceptor [10,31]. One of the most simple, efficient, and studied photosensitizers is $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) [10,32]. Absorption of a visible light photon with $\lambda = 450$ nm transfers this complex to an exited state which easily loses electron to produce $[Ru(bpy)_3]^{3+}$, a strong oxidant. Sacrificial electron acceptor is required for this scheme of action. The most common known is persulfate, $S_2O_8^{2-}$ [10,33]. Finally, a buffer is required for keeping the pH value at the proper level. The overall catalytic system for the screening of the WOC activity is depicted in Scheme 1. A large series of metal complexes have been tested as WOCs using this scheme, mainly compounds of ruthenium and iridium [10,31,34]. However, the first-row transition metals, as the more abundant and less expensive ones, also represent a great interest form a practical point of view [35–38]. In this review we focus on the cobalt polynuclear complexes as the catalysts for light-driven water oxidation, with special attention to their stability under the studied catalytic conditions.



Scheme 1. General functioning mechanism of the light driven water oxidation system $[Ru(bpy)_3]^{2+}/Catalyst/S_2O_8^{2-}$.

Despite the impressive number of H₂-evolving water splitting (reduction) cobalt catalysts [39], the field of cobalt-catalysed water oxidation has risen only during the last decade. The activity of simple cobalt compounds (salts and oxides) in the catalytic chemical water oxidation with [Ru(bpy)]³⁺ or other strong oxidants has been known for some time [10], but did not attract much attention until 2008, where Kanan and Nocera presented the Co-P electrocatalytic film for water oxidation formed in situ from aqueous Co²⁺ in phosphate buffer at neutral pH [40]. In 2009, Jiao and Frei reported the light driven system with the Co_3O_4 nanoparticles as a WOC, operating at mild conditions (room temperature and pH 5.8) [41]. The system [Ru(bpy)₃]Cl₂/Co₃O₄/Na₂S₂O₈ shows the TOF (turnover frequency, moles of product produced per mol of catalyst per a certain period of time) of more than 1000 s^{-1} per Co_3O_4 nanoparticle. For comparison, the TOF of the natural PSII is estimated at 100 to 400 s⁻¹ level in live cells and 1000 s^{-1} in vitro [42]. Just one year after, in 2010, a study was published that highlighted a stable carbon-free WOC based on tetranuclear cobalt moiety $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-1}$ for chemical water oxidation with $[Ru(bpy)]^{3+}$, allowing the TOF of 5 s⁻¹ and TON (turnover number, moles of product per mol of catalyst) of 78, and then (in 2011) for light-driven oxidation to reach the TON of > 220 [43,44]. Remarkably, in the same year, 2011, Stracke and Finke reported that under the conditions of electrocatalytic water oxidation, this compound releases Co^{2+} ions to form CoO_x as an active catalyst [45]. These reports caused considerable interest in the field but also demonstrated the complexity of the problem of clear identification of the true WOC.

2. Mono- and Binuclear Cobalt Complexes

The complex $[Co(L^1)]$ (1) (Figure 2) with Schiff base ligand H_2L^1 (N,N'-bis(salicylidene) ethylenediamine, known also as "salen"), shows high TON and TOF values, as well as the quantum yield of O₂, using $[Ru(bpy)_3](ClO_4)_2$ as a photosensitizer (Table 1) [46]. When the ClO_4^- anion was replaced with Cl^- or SO_4^{2-} one the TON drops to ca. 780 and 190, respectively. Complex 1 retains its activity when [Ru(bpy)₃](ClO₄)₃ was used as a terminal chemical oxidant, although showing lower catalytic parameters (Table 1). Further investigations disclosed that 1 was a pre-catalyst and its catalytic activity was associated to cobalt nanoparticles formed during the photocatalysis. According to ESI-MS (electrospray mass spectrometry) and DLS (dynamic light scattering) measurements, complex 1 was shown to be stable in the presence of the main components of the catalytic system, in the absence of light. However, after illumination the presence of nanoparticles of various sizes (1–1000 nm) were detected by the DLS method. Moreover, no signals from salen ligand were observed by ¹H NMR, suggesting its complete decomposition. The precipitate formed after the illumination was recovered and used again as a catalyst, showing somewhat lower water oxidation activity than 1 (40.9 and 54.6% of the yield of O_2 based on $S_2O_4^{2-}$, respectively). The cobalt nitrate was tested as WOC (31a, Table 1) under the same conditions as above, showing nearly the same TON as 1 as well as similar O_2 accumulation kinetics [46]. Cobalt salts form CoO_x nanoparticles in the $[Ru(bpy)_3]^{2+}/S_2O_8^{2-}$ water oxidation systems (31–33, Table 1), providing a non-direct proof for the instability of 1, which appears to be just a pre-catalyst.

N	Core	(Pre)catalyst	O ₂ Evolution, μmol/μM	TON ¹	TOF ² , s ⁻¹ ,	QE ³ , %	λ^4 , nm	Irradiation Source	рН	NP ⁵	Anion ⁶	[cat] ₀ , μΜ	Ref.
1a	Co ₁	$[Co^{II}(L^1)]$	13.7/1366	854	6.4	38.6	>420	LED, 5.1 mW/cm^2	9	+	ClO ₄	1.6	[46]
1b	Co ₁	$[Co^{II}(L^1)]$	n.d. ⁷	194	2.0	-	-	Chemical oxidation with [Ru(bpy) ₃] ³⁺	9	n.d. 7	ClO ₄	n.d.	[46]
2	Co ₁	[Co ^{II} (TPPS)]	12.2/1220	122	0.17	n.d.	400-800	Xe lamp, 300 W	11	-	NO ₃	10	[47]
3	Co ₁	$[Co^{II}(L^2)(H_2O)_2](ClO_4)_2$	0.55/67	335	n.d.	n.d.	475	Hg arc lamp, 500 W	8	-	Cl	0.2	[48]
4	Co ₁	[Co ^{II} (bpy) ₂ (H ₂ O)](ClO ₄) ₂	0.34/41	206	n.d.	n.d.	475	Hg arc lamp, 500 W	8	n.d.	Cl	0.2	[48]
5a	Co ₁	$[Co^{II}(L^3)(H_2O)](ClO_4)_2$	5.4/2700	54	n.d.	32	>420	Xe lamp, 500 W	8	+	ClO ₄	50	[49]
5b	Co ₁	$[Co^{II}(L^3)(H_2O)](ClO_4)_2$	0.9/450	9	n.d.	n.d.	>420	Xe lamp, 500 W	8	n.d.	Cl	50	[49]
6a	Co ₂	$[\text{Co}^{\text{III}}_2(\mu\text{-OH})_2(\text{TPA})_2](\text{ClO}_4)_4$	9.3/1855	742	n.d.	44	420	Xe lamp	9.3	-	ClO_4	2.5	[50]
6b	Co ₂	$[Co^{III}_2(\mu-OH)_2(TPA)_2](ClO_4)_4$	5.4/1080	2.7	n.d.	n.d.	420	Xe lamp	9.3	-	ClO ₄	400	[50]
7a	Co ₂	$[(TPA)Co^{III}(\mu-OH)(\mu-O_2)Co^{III}(TPA)](ClO_4)_3$	0.1/99	58	1.4	n.d.	470	LED, 820 µE/s	8	-/+	ClO ₄	5	[51]
7b	Co ₂	$[(TPA)Co^{III}(\mu-OH)(\mu-O_2)Co^{III}(TPA)](ClO_4)_3 + 1 \text{ eq. bpy}$	0/0	0	0	0	470	LED, 150 mW/cm ²	8	n.d.	ClO ₄	5	[52]
8a	Co ₂	$[(L^4)Co^{III}(\mu\text{-}OH)(\mu\text{-}O_2)Co^{III}(L^4)](ClO_4)_3$	35/2333	233	n.d.	n.d.	>420	LED, 5.0 mW/cm^2	9	n.d.	Cl	10	[53]
8b	Co ₂	$[(L^4)Co^{III}(\mu-OH)(\mu-O_2)Co^{III}(L^4)](ClO_4)_3 + 5 \text{ eq. bpy}$	0/0	0	0	0	>420	LED, 5.0 mW/cm^2	9	n.d.	Cl	10	[53]
9	Co ₄	$[\text{Co}^{\text{III}}_4\text{O}_4(\text{OAc})_4(\text{py})_4]$	16/1143	>40	0.02	n.d.	>395	Arc lamp, 250W, 2 mW/cm ²	7	n.d.	Cl	330	[54]
10	Co ₄	$[Co^{III}_4O_4(OAc)_4(p-py-OCH_3)_4]$	5.0/2520	140	~0.04	80	>400	Halogen lamp	8	n.d.	Cl	18	[55]
11a	Co ₄	$[Co^{II}_4(L^5)_4(OAc)_4(H_2O)_2]$	15.5/1940	20	1.8	n.d.	470	LED, 26.1 mW/cm ²	7	-	Cl	97	[56]
11b	Co ₄	$[Co^{II}_4(L^5)_4(OAc)_4(H_2O)_2]$	14.4/1800	35	4.4	n.d.	470	LED, 26.1 mW/cm ²	8	-	Cl	60	[56]
11c	Co ₄	$[Co^{II}_4(L^5)_4(OAc)_4(H_2O)_2]$	13.4/1680	28	7	n.d.	470	LED, 26.1 mW/cm ²	9	-	Cl	60	[56]
12	Co ₄	$[Co^{III}_4O_4(OAc)_2(bpy)_4](ClO_4)_2$	n.d.	n.d.	0.02	n.d.	>380	LED	8	n.d.	Cl	0.2	[57]
13a	Co ₄	[Co ^{III} 4O4(OAc)4(py)4], crude sample	0.3/167	0.5	n.d.	n.d.	>400	Hg/Xe arc lamp, 1000 W	7	n.d.	Cl	330	[58]
13b	Co ₄	$[Co^{III}_4O_4(OAc)_4(py)_4]$ after purification	0.06/31	0.09	$2.3 imes 10^{-4}$	n.d.	>400	Hg/Xe arc lamp, 1000 W	7	n.d.	Cl	330	[58]
14a	Co ₄	$[Co^{II}_4(L^6)_4(OAc)_2(H_2O)_2](ClO_4)_2$	9.6/1200	96	1.2	n.d.	470	LED, 26.1 mW/cm ²	8.5	-	Cl	12.5	[59]
14b	Co ₄	$[Co^{II}_{4}(L^{6})_{4}(OAc)_{2}(H_{2}O)_{2}](ClO_{4})_{2}$	16.0/2000	20	0.24	n.d.	470	LED, 26.1 mW/cm ²	8.5	-	Cl	100	[59]
15	Co _{4-x} Ni _x	[Co ^{II} _{1.15} Ni ^{II} _{2.85} (L ⁶) ₄ (OAc) ₂ (H ₂ O) ₂](ClO ₄) ₂	5.5/690	6.9	0.1	n.d.	470	LED, 26.1 mW/cm ²	8.5	n.d.	Cl	100	[59]
16	Co ₃ Ho	$[Co^{II}_{3}Ho(L^{5})_{4}(OAc)_{5}(H_{2}O)]$	13.0/1630	163	5.8	n.d.	450	LED, 26.1 mW/cm ²	8	-	Cl	10	[60]
17	Co ₃ Er	$[Co^{II}_{3}Er(L^{5})_{4}(OAc)_{5}(H_{2}O)]$	16.9/2110	211	5.7	n.d.	450	LED, 26.1 mW/cm ²	8	-	Cl	10	[60]
18	Co ₃ Tm	$[\text{Co}^{\text{II}}_{3}\text{Tm}(\text{L}^{5})_{4}(\text{OAc})_{5}(\text{H}_{2}\text{O})]$	7.4/920	92	5.3	n.d.	450	LED, 26.1 mW/cm ²	8	-	Cl	10	[60]
19	Co ₃ Yb	$[\mathrm{Co}^{\mathrm{II}}_{3}\mathrm{Yb}(\mathrm{L}^{5})_{4}(\mathrm{OAc})_{5}(\mathrm{H}_{2}\mathrm{O})]$	12.8/1600	160	6.8	n.d.	450	LED, 26.1 mW/cm ²	8	-	Cl	10	[60]
20a	Co ₄	$\{Co^{III}_4O_4(OAc)_3(py)_4\}\{(L^7)Ru(bpy)_2\}$	0.15/75	5	7×10^{-3}	n.d.	>400	Xe lamp, 300 W	7	n.d.	Cl	15	[61]
20b	Co ₄	$[\mathrm{Co}^{\mathrm{III}}{}_4\mathrm{O}_4(\mathrm{OAc})_4(\mathrm{py})_4] + 1 \text{ eq. } [\mathrm{Ru}(\mathrm{bpy})_3]\mathrm{Cl}_2$	n.d.	2	5×10^{-3}	n.d.	>400	Xe lamp, 300 W	7	n.d.	Cl	15	[61]
21	Co ₄	$\{Co^{III}_{4}O_{4}(OAc)_{2}(py)_{4}\}_{2}\{(L^{8})Ru(bpy)_{2}\}_{2}$	0.74/360	24	0.02	n.d.	>400	Xe lamp, 300 W	7	n.d.	Cl	15	[61]
22a	Co ₄	$Na_{10}[Co_4(H_2O)_2(VW_9O_{34})_2]$	n.d./0.15	300	>1600	-	-	Chemical oxidation with [Ru(bipy) ₃] ³⁺	9	-	ClO ₄	0.5	[62]
22b	Co ₄	$Na_{10}[Co_4(H_2O)_2(VW_9O_{34})_2]$	3.0/1484	742	4	61	455	LED, 135 mW/cm^2	9	-	Cl	2.0	[62]
22c	Co ₄	$Na_{10}[Co_4(H_2O)_2(VW_9O_{34})_2]$	1.7/842	4210	n.d.	48	455	LED, 135 mW/cm^2	9	-	Cl	0.2	[62]
23	Co ₄	$[Co_4(H_2O)_4(HL^9)_2(L^9)_2]$	13.2/1324	662	0.03	n.d.	>420	Xe lamp, 300 W, 26.4 mW/cm ²	9	-	ClO_4	2	[63]

Table 1. Selected catalytic parameters for the catalysts 1–33 in oxidation of water using $[Ru(bpy)_3]^{2+}$ as a photosensitizer and $S_2O_8^{2-}$ as a sacrificial electron acceptor.

Table 1. Cont.

N	Core	(Pre)catalyst	O2 Evolution, µmol/µM	TON ¹	TOF ² , s ⁻¹ ,	QE ³ , %	λ^4 , nm	Irradiation Source	pН	NP ⁵	Anion ⁶	[cat] ₀ , μΜ	Ref.
24a	Co ₆	$K_{12}[Co(L^9)]_6$	1.1/113	1125	35.3	5.9	460	LED, 33.8 mW/cm ²	9	n.d.	Cl	0.1	[64]
24b	Co ₆	$K_{12}[Co(L^9)]_6$	4.4/435	4350	162.6	27.1	460	LED, 33.8 mW/cm ²	9	n.d.	ClO ₄	0.1	[64]
24c	Co ₆	$K_{12}[Co(L^9)]_6$	11.7/1169	167	4.4	51.5	460	LED, 33.8 mW/cm ²	9	n.d.	Cl	7	[64]
25	Co ₇	$Na_{12}[{Co^{II}_{7}As_{6}O_{9}(OH)_{6}}(SiW_{9}O_{34})_{2}]$	2.3/115	115.2	0.14	n.d.	>420	Xe lamp, 300W	8	-	Cl	1	[65]
26a	Co ₇	$[Co_{5}^{II}Co_{2}^{III}(mdea)_{4}(N_{3})_{2}(CH_{3}CN)_{6}(OH)_{2}(H_{2}O)_{2}](ClO_{4})_{4}$	10.7/1070	43	n.d.	n.d.	450	LED	9	n.d.	Cl	25	[66]
26b	Co ₇	$[Co_{5}^{II}Co_{2}^{III}(mdea)_{4}(N_{3})_{2}(CH_{3}CN)_{6}(OH)_{2}(H_{2}O)_{2}](ClO_{4})_{4}$	22/2200	88	n.d.	n.d.	450	LED	9	n.d.	ClO_4	25	[66]
26c	Co ₇	$[Co^{II}_{5}Co^{III}_{2}(mdea)_{4}(N_{3})_{2}(CH_{3}CN)_{6}(OH)_{2}(H_{2}O)_{2}](CIO_{4})_{4}$	10.5/1050	210	n.d.	n.d.	450	LED	9	n.d.	Cl	5	[66]
27a	Co ₈	K ₈ Na ₈ [(SiW ₉ O ₃₄) ₂ Co ₈ (OH) ₆ (H ₂ O) ₂ (CO ₃) ₃]	16.4/1090	545	3.1	35.8	>420	LED, 5.1 mW/cm^2	9	-	Cl	2	[67]
27b	Co ₈	K ₈ Na ₈ [(SiW ₉ O ₃₄) ₂ Co ₈ (OH) ₆ (H ₂ O) ₂ (CO ₃) ₃]	10.8/718	1436	10	28.8	>420	LED, 5.1 mW/cm^2	9	n.d.	Cl	0.5	[67]
28	Co ₉	$K_{16}[Co_9(H_2O)_6(OH)_3(PW_9O_{34})_3]$	1.0/67	10	5×10^{-3}	n.d.	>375	Tungsten lamp, 150 W, 90 mW/cm ²	8	n.d.	n.d.	6.6	[68]
29a	Co ₁₅	$Na_5[Co_6(H_2O)_{30}\{Co_9Cl_2(OH)_3(H_2O)_9(SiW_8O_{31})_3\}]$	3.1/207	53	$21 imes 10^{-3}$	n.d.	>375	Tungsten lamp, 150 W, 90 mW/cm ²	8	n.d.	n.d.	3.4	[68]
29b	Co ₁₅	$Na_5[Co_6(H_2O)_{30}\{Co_9Cl_2(OH)_3(H_2O)_9(SiW_8O_{31})_3\}]$	4.1/273	28	19×10^{-3}	5.5	450	LED, 7 mW	8	n.d	n.d.	9.8	[68]
30	Co ₁₆	$Na_{22}Rb_{6}[\{Co_{4}(OH)_{3}PO_{4}\}_{4}(PW_{9}O_{34})_{4}]$	2.0/133	37	$24 imes 10^{-3}$	n.d.	>375	Tungsten lamp, 150 W, 90 mW/cm ²	8	n.d.	n.d.	3.6	[68]
31a	Co ₁	$Co(NO_3)_2$	12.2/1219	762	n.d.	n.d.	>420	LED, 5.1 mW/cm^2	9	+	ClO_4	1.6	[46]
31b	Co ₁	$Co(NO_3)_2$	5.2/2600	52	n.d.	n.d.	>420	Xe lamp, 500 W	8	+	ClO_4	50	[49]
31c	Co ₁	Co(NO ₃) ₂	4.6/310	4.3	1.92×10^{-3}	11	450	LED, 42 mW	8	-	Cl	72	[69]
31d	Co ₁	Co(NO ₃) ₂	11.1/1112	139	n.d.	n.d.	>420	Xe lamp, 300 W, 26.4 mW/cm ²	8	+	ClO ₄	8	[63]
31e	Co ₁	$Co(NO_3)_2$	19.5/1952	244	n.d.	n.d.	>420	Xe lamp, 300 W, 26.4 mW/cm ²	9	+	ClO_4	8	[63]
31f	Co ₁	Co(NO ₃) ₂	3/300	150	n.d.	n.d.	>420	Xe lamp, 300 W, 26.4 mW/cm ²	8	+	ClO_4	2	[63]
32a	Co ₁	$Co(ClO_4)_2$	0.4/400	570	19	n.d.	470	LED, 150 mW/cm ²	8	+	ClO_4	0.7	[52]
32b	Co ₁	Co(ClO ₄) ₂	0.25/250	500	16	n.d.	470	LED, 150 mW/cm ²	8	+	ClO ₄	0.5	[52]
32c	Co ₁	$Co(ClO_4)_2 + 8$ eq. bpy	0/0	0	0	n.d.	470	LED, 150 mW/cm ²	8	+	ClO_4	0.5	[52]
33a	Co ₁	Co(OAc) ₂	5.4/680	7	n.d.	n.d.	470	LED, 26.1 mW/cm ²	7	+	Cl	250	[56]
33b	Co ₁	Co(OAc) ₂	9.2/924	132	3.1	36.1	460	LED, 33.8 mW/cm ²	9	n.d.	ClO ₄	7	[64]

¹ Moles of product per mol of catalyst; ² Moles of product produced per mol of catalyst per a certain period of time; ³ Quantum efficiency, moles of O₂ produced per moles of absorbed photons; ⁴ Irradiation wavelength, as reported; ⁵ Formation of nanoparticles; ⁶ anion of the [Ru(bpy)₃]²⁺ photosensitizer; ⁷ no data.



Figure 2. Structures of complexes 1-5. Color scheme: Co, pink; O, red; N, blue; S, yellow; C, grey.

Complexes of porphyrin ligands are known to catalyze a wide range of reactions due to the pronounced stability of porphyrins, their redox activity, and ability to stabilize high-valent metal-oxo species of iron, manganese, ruthenium, and other metals [70–72]. A series of the water-soluble porphyrin complexes of cobalt have been tested as WOCs. The best results were obtained using the catalyst [Co(TPPS)] (2) with porphyrin ligand TPPS (meso-tetrakis(4-sulfophenyl)porphyrin) (Figure 2), reaching the TOF value of 0.17 s^{-1} at pH 11 [47]. At lower or higher pH, TOF did not exceed 0.05 s^{-1} . From the second order dependence of the initial rate of O_2 formation on the $[2]_0$, as well as from the DFT calculations, it was proposed that two molecules of **2** are required for completion of the water oxidation catalytic cycle. The proposed catalytic cycle presumes coupling of the Co-O• radicals as the principal mechanistic step, corresponding to the so-called I2M type of mechanisms (Scheme 2) [7]. One may notice, however, that for the electrocatalytic water oxidation catalyzed by cobalt porphyrins, the water nucleophilic attack (WNA) mechanism was proposed [73]. No nanoparticles formation was observed by DLS measurements. Appearance of the Soret band of porphyrin after mixing of $[Ru(bpy)_3]^{3+}$ with 2 also suggests that 2 is responsible for the catalytic activity. An unusual feature of this catalytic system is the use of nitrate salt of the $[Ru(bpy)_3]^{2+}$ photosensitizer (Table 1) instead of common chloride or perchlorate ones.

Two complexes, **3** and **4**, with polypyridine ligands (Figure 2) were tested as WOCs and revealed similar activities (Table 1) [48]. Chemical oxidation with $[Ru(bpy)]^{3+}$ was performed resulting on TON values of 160 and 70 for **3** and **4**, respectively. No formation of cobalt oxide nanoparticles or leaching of the cobalt ions was observed under catalytic conditions (both in light-driven and chemical oxidations), as evidenced by ESI-MS and DLS tests. The authors proposed the existence of two active intermediates, which ratio is defined by relative stability of the molecular intermediate [48]. One may notice that very low concentrations of the catalysts in the case of **3** and **4** (0.2 μ M) may prevent correct determination of the nanoparticles or other decomposition products by conventional methods.



Scheme 2. Proposed pathways for the O₂ formation in the water oxidation catalyzed by 2.

A series of mononuclear cobalt complexes with polydentate N-donor ligands was prepared and studied as catalysts in the light-driven water oxidation. The most active complex $[Co(L^3)]$ (5) having tris(N,N'-(dimethylamino)ethyl)amine ligand (Figure 2) showed the TON values up to 54 and quantum yield of O₂ up to 32% (5a, Table 1) [49]. Very similar results were obtained for Co(NO₃)₂ as pre-catalyst (31b, Table 1), suggesting decomposition of complex 5 under catalytic conditions. Formation of nanoparticles with sizes ranging from 10 to 50 nm was confirmed by DLS and TEM (transmission electron microscopy) for the case of 5. The size of particles and their aggregation behavior were different for 5 and Co(NO₃)₂. Moreover, the dependence of the yield of O₂ on the pre-catalyst concentration showed no changes at $[Co(NO_3)_2]_0 > 1$ mM, while for $[5]_0 > 0.1$ mM the catalytic activity showed rapid decay until no evolution of O_2 at $[5]_0 = 2.5$ mM. Formation of CO_2 in the catalytic system $[Ru(bpy)_3]^{2+}/5/S_2O_8^{2-}$, with elevated concertation of persulfate (50 mM), unambiguously pointed out the oxidation of organic ligand of 5. The authors concluded that although complex 5 (and other complexes of the series) acts as a pre-catalyst, the nature of the ligand influences the structure and composition of the oxide nanoparticles formed and therefore the catalytic activity as well [49]. As a final remark, one may notice a strong influence of the nature of anion of [Ru(bpy)₃]²⁺ photosensitizer, where perchlorate system (5a) is six times more active than the chloride one (5b).

The cobalt complex $[Co_2(\mu-OH)_2(TPA)_2](ClO_4)_4$ (6) with tris(2-pyridylmethyl)amine (TPA) was synthesized by dimerization of the mononuclear complexes $[Co^{III}(TPA)Cl_2](ClO_4)$ in the presence of AgClO₄ as a halogen acceptor [50]. The crystal structure of **6**, features a binuclear core where metal atoms are mediated by the bridging oxido ligands (Figure 3). The highest TON of 742 was obtained for low concentration of the catalyst (**6a**, Table 1). Increase of [**6**]₀ led to lower evolution of O₂ (**6b**). Chemical water oxidation with $[Ru(bpy)]^{3+}$ showed the TON of 4.3. According to DFT calculations, the active species are formed from the two-electron oxidation of **6** (Scheme 3). As evidenced by the ¹H NMR and DLS experiments performed for [**6**]₀ = 0.4 mM, complex **6** is stable during the photocatalytic reaction. Also, no CO₂ evolution, attributable to TPA ligand oxidation, was detected. These results are in accord with the ones observed for the TPA family of ligands in various oxidative processes. For instance, iron complexes with TPA are known to stabilize Fe^{IV} and Fe^V species capable of abstracting H atoms from sp³ C–H bonds [74,75].



Figure 3. Structures of complexes **6–8**. Color scheme: Co, pink; O, red; N, blue; S, yellow; C, grey. Co–O–Co bonds are highlighted by yellow.



Scheme 3. Proposed pathways for the O_2 formation in the water oxidation catalyzed by 6.

In contrast to **6**, obtained from the Co^{III} starting material, dimerization of $[Co^{II}(TPA)CI]CI$ complexes in the presence of LiClO₄ in open air, led to in situ oxidation of cobalt to Co³⁺ and formation of the Co–O–O–Co bridge in the complex $[(TPA)Co(\mu-OH)(\mu-O_2)Co(TPA)](ClO_4)_3$ (7) (Figure 3) [51]. The compound was found to be stable at ambient conditions and showed moderate activity as a WOC at pH 8 with TON = 58. The authors performed DLS measurements and concluded that no CoO_x nanoparticles are formed during the photocatalytic reaction, while the control DLS experiment using Co(ClO₄)₂ as a catalyst revealed nanoparticles with ca. 100 nm size after irradiation. However, just two years later these results were reinvestigated by a different group of authors [52]. The use of an extended set of methods disclosed that the catalytic system based on complex 7 is in fact heterogeneous and contains CoO_x nanoparticles. Specifically, the water oxidation activity using the pre-catalyst 7 was completely suppressed when adding chelating ligands such as EDTA (ethylenediaminetetraacetic acid) or bpy (Figure 4a). The presence of just 0.1 mM of EDTA led to zero yields of O₂ for 0.5 mM of 7. The test with bipyridine requires its larger amounts, but one equivalent of bpy (5 μ M of bpy per 5 μ M of 7) is enough for quenching the catalytic activity of 7 [52]. Such behavior is consistent with that observed for Co(ClO₄)₂ salt as a catalyst, which activity at 0.7 μ M concentration (**32a**, Table 1; Figure 4b) is

completely quenched with eight equivalents of bpy (**32b**, Table 1). A question appears, namely, why earlier DSL measurements did not detect nanoparticles presumably formed upon degradation of complex 7? A general explanation could be the different experimental conditions in these cases. It was mentioned that the DLS method might not detect small particles (at low amounts) formed in the course of reaction. Also, as can be seen from the systems **31** and **32** (Table 1), cobalt cations act as very efficient pre-catalysts at micromolar concentrations. Thus, even a small leaching of cobalt cations (captured by EDTA and bpy) from the initial coordination compound may be responsible for the pronounced catalytic activity, initially associated to the complex. In any case, these studies clearly demonstrate that the conclusion about the catalyst stability should not be made based on a single experimental method, such as DLS.



Figure 4. Accumulations of the oxygen in the course of water oxidation catalyzed by complex 7 (**a**) or $Co(ClO_4)_2$ (**b**), in the presence of various amounts of bipyridine (bpy) chelating agent. Adapted with permission from [52], American Chemical Society, 2016.

By reacting of the Schiff base ligand, N,N-bis(pyridin-2-ylmethylene)ethane-1,2-diimine (L⁴), and $Co(ClO_4)_2$ in excess of pyridine the binuclear complex $[(L^4)Co^{III}(\mu-OH)(\mu-O_2)Co^{III}(L^4)](ClO_4)_3$ (8) has been prepared [53]. The structure of its core is similar to that observed for 7 (Figure 3). The light-driven water oxidation activity was studied by the independent group of authors, revealing TON values and oxygen concentrations much higher than those for 7 (Table 1). However, the tests performed in the presence of bpy ligand showed complete suppression of the catalytic activity with five equivalents of bpy (7b, Table 1), indicating that the observed activity could be associated to the free cobalt cations, rather than complex 7.

3. Tetranuclear Cubanes Co_4O_4 or $Co_{4-x}M_xO_4$

In 2011 McCool at al. reported the water oxidation catalytic activity of the tetranuclear complex $[Co^{III}_4O_4(Ac)_4(py)_4]$ (9) [54]. This coordination compound was known earlier, and was also studied as a catalyst for the alcohols oxidation [76]. Its structure (Figure 5) represents a cubane core $Co_4(\mu_3-O)_4$, resembling that found in the PSII protein (CaMn₃O₄). The TOF of 0.02 s⁻¹ exhibited by 9 for the light-driven oxidation was among, as of 2011, the highest known, resulting in high interest in the tetranuclear cobalt complexes as WOCs. The stability of the catalyst under the conditions of experiment was confirmed by the ¹H NMR (constant signals from acetate and pyridine ligands). Furthermore, the authors studied dependence of the lag time on the catalyst concentration. Lag period is expected when a catalyst undergoes transformations to active species (such as CoO_x nanoparticles) after irradiation begins, thus a lag time smaller than that for cobalt salt suggests the stability of the catalyst. The catalytic system based on complex 9 showed small lag time (less than 20 s for [9]₀ ~ 4 mM), and this

was associated by the authors to low oxidant/catalyst ratio, while the cobalt salt showed a lag time of almost 200 s under the same conditions [54].



Figure 5. Structures of complexes **9**, **11**, **12**, **14**, and **16–19** with the schemes of respective N-donor ligands. Color scheme: Co, pink; Ln, green; O, red; N, blue; C, grey. M–O–M bonds are highlighted by yellow.

The water oxidation activity of a series of related complexes $[Co^{III}_4O_4(OAc)_4(p-py-X)_4]$ having para-substituted pyridine (X = H, Me, *t*-Bu, OCH₃, Br, COOCH₃, CN) ligands has been reported in 2012 [55]. The nature of the substituent had strong influence on the catalytic activity, with the quantum yields (yield of oxygen based on the photon flux) ranging from 10% (for *t*-Bu) to 80% (for OCH₃; **10**, Table 1), suggesting the molecular nature of catalytically active species. In contrast to most of the other studies, 1:1 mixture of water:acetonitrile was used as a solvent.

Replacement of pyridine with 2-(hydroxymethyl)pyridine ligand (HL⁵), which provides oxygen donor atoms, has led to the formation of cubane complex $[Co^{II}_4(L^5)_4(OAc)_4(H_2O)_2]$ (11) where cobalt has +2 oxidation state (Figure 5), as reported one year after, in 2013 [56]. Another difference from complexes 9 and 10 is the presence of water molecules coordinated to cobalt centers. Water ligands take an important place in the structure of the active centers of PSII (Figure 1), thus the authors indicate that the structure of complex 11 is close to that of the PSII Mn₄CaO₄ cubane. Studies of methanol and water solutions of **11** by ESI-MS and pH-dependent UV-Vis titration disclosed that water ligands remain intact at neutral pH, becoming labile in the alkali media. The presence of labile water represents the main feature of 11 comparing to 9 and 10, where, in the absence of coordinated water molecules, the protonation–deprotonation may occur at the Co_4O_4 core. Dependences of the TON and TOF in the course of catalytic water oxidation on pH were studied, disclosing that the highest TON of 35 is achieved at pH 8 (**11b**, Table 1) and the highest TOF of 7.0 s⁻¹ at pH 9 (**11c**, Table 1). Stability of the core of 11, under catalytic conditions, was investigated by the cyclic voltammetry (CV) experiments, suggesting that the structure of the compound does not undergo degradation. No nanoparticles in the catalytic solutions after 60 min of visible light irradiation were detected by the DLS method. In the comparative test with Co(OAc)₂, formation of the two fractions of nanoparticles (of ca. 5 and 120 nm

diameter) under the same conditions was observed. Furthermore, significant difference in the lag times between 11 and $Co(OAc)_2$ catalysts has been observed: While cobalt acetate shows a lag period of 25 s, complex 11 exhibits a much shorter time (ca. 5 s), which does not depend on the catalyst concentration.

A series of bi-, tri-, and tetranuclear complexes with pyridine and bipyridine ligands have been tested as the WOCs by Smith et al. in 2014 [57]. While the complexes containing two or three metal centers were found to be catalytically inactive, the tetranuclear compound bearing cubane core $[Co^{III}_4O_4(OAc)_2(bpy)_4](ClO_4)_2$ (12) (Figure 5) showed the activity with maximum TOF of 0.05 s^{-1} , achieved at $[11]_0 = 0.02 \mu$ M. At higher concentrations of the catalyst, the TOF drops until 0.02 s^{-1} (Table 1). The catalyst 9 was also tested under the same conditions, showing a bit higher activity, with a maximum TOF of 0.09 s^{-1} [57]. The catalytic mixture containing 11 was analyzed by means of the ESI-MS spectroscopy, revealing the presence of the unaltered complex 11 at 521 m/z. The authors interpreted this observation, with the support of 1H NMR data, as evidence that 11 is a truly molecular WOC. No DLS experiments data were reported.

In 2014, the group of Nocera reinvestigated the water oxidation properties of complexes **9** and **10** [58]. It was demonstrated that the catalytic activity previously associated to the cubane complexes is, in fact, exhibited by the small amounts of Co²⁺ impurities present in the samples. The ¹H NMR spectra of the crude samples of **9** and **10** showed many small peaks. Furthermore, thin layer chromatography disclosed the presence of a few bands in addition to that of the complexes. Purification of the samples using the column chromatography afforded the products with clear ¹H NMR spectra. The light-driven water oxidation tests showed that purified samples of **9** possesses ca. five times lower activity than the crude ones (entries **13a** and **13b**, Table 1). The exact nature of the Co²⁺ impurities was not identified. It was mentioned that they do not elute on silica and act as a precursor for a heterogeneous oxygen evolving catalyst. Notably, even after purification, complex **9** reveals detectable water oxidation activity (entry **13b**, Table 1).

A series of cubane cobalt Co₄O₄ (14) and mixed-metal Co_{4-x}Ni_xO₄ (15) complexes having bipyridine-like ligand was reported in 2017 [59]. The base complex $[Co^{II}_4(L^6)_4(OAc)_2(H_2O)_2](ClO_4)_2$ (14) was prepared starting from the pro-ligand di(2-pyridyl)ketone, which is hydrolyzed to produce the ligand L⁶ (Figure 5). Complex 14 revealed moderate activity in the water oxidation with maximum TON of 96 (Table 1) at pH 8.5. In general, the catalytic parameters exhibited by 14 are close to other cobalt cubane complexes (9–13). No nanoparticles formation was observed according to the DLS experiments. The possibility of significant cobalt leaching was rejected by applying the Chelex[®] resin able to capture free metal ions: only a negligible drop of catalytic activity was observed in the case of 14, while a simple cobalt salt showed 66% suppression caused by the resin trap. The presence of cobalt in the +2 oxidation state allowed isomorphic substitution of cobalt ions with nickel ones to obtain a series of Co_{4-x}Ni_xO₄ cubane complexes with maximum x = 2.85 (not including pure nickel compound with x = 4), bearing the same structures. The catalytic activity in the water oxidation gradually dropped with the increase of nickel portion, showing the TON and TOF ca. three times lower than for pure cobalt complex. The complex Ni₄O₄ did not show any notable catalytic activity under the same conditions [59].

Substitution of one of the metal positions with lanthanide led to a series of Co_3LnO_4 cubane complexes $[Co^{II}_3Ln(L^5)_4(OAc)_5(H_2O)]$ (16–19) with 2-(hydroxymethyl)pyridine) ligand (HL⁵) [60]. Compounds of this series were firstly synthesized by mixing cobalt and lanthanide acetates in stoichiometric ratio of 3:1 and characterized by X-ray diffraction [77]. The modified synthetic protocol using Co:Ln ratio of 2.3:1 afforded Co₃Ln compounds, where Ln = Ho, Er, Tm, and Yb [60]. All complexes show the best performance at pH = 8, being slightly less active at pH = 9 and considerably less active at pH = 7. Erbium complex is the most active with TON > 200, while the compound containing thulium shows the weakest results (Table 1). The authors followed a special workflow designed for clear identification of the complexes **16–19** as the water oxidation catalysts. The most important evidence was obtained from the DLS tests (no nanoparticles formation was detected) and trapping of "free" Co²⁺ ions with EDTA or Chelex[®] resin (no influence on the catalytic parameters

observed). Stability of the tetranuclear cores in solution was confirmed by EXAFS, XANES and ESI-MS tests. The coordinated water molecule undergoes rapid exchange with solvent water, as evidenced by the tests in CD_3CN and CD_3CN/D_2O mixture, monitored by FT-IR. The authors account that lanthanide Ln^{3+} serves as a catalytic promoter, possibly working in analogy to Ca^{2+} in the natural $CaMn_3O_4$ OEC [60].

Typically, the components of the model catalytic system $[Ru(bpy)]^{2+}/catalyst/S_2O_8^{2-}$ are dissolved separately and do not form aggregates in a solution. In such system the electron transfer between the components is strongly influenced by their concentrations. This obstacle could be overcome by joining the photosensitizer, catalyst, and electron acceptor into one module, as it is found in a natural PSII complex. Such an approach is exemplified by the supramolecular assemblies $\{Co_4O_4(OAc)_3(Py)_4\}\{(L^7)Ru(bpy)_2\}\$ and $\{Co_4O_4(OAc)_2(Py)_4\}_2\{(L^8)Ru(bpy)_2\}_2\$ (20 and 21, respectively, Table 1) (L^7 = bpy-4-CH₃,4'-COOH; L^8 = bpy-4-COOH, 4'-COOH) [61], which include two well-studied components: Ruthenium photosensitizer and Co₄O₄ cubane WOC (similar to 9). In these compounds, chemical linkage is realized through the modification of bipyridine ligand, attaching to them one or two carboxylic groups (Scheme 4). The integrity of the structures of **20** and **21** is supported by ESI-MS and ¹H-¹H COSY NMR spectroscopes. Assemblies 20 and 21 have been tested in the light-driven water oxidation (Figure 6) using a rather low concentration of the catalyst of 15 μ M (calculated per Co₄O₄) cubane), showing the TON value of 25 in case of compound 21 (Table 1). The results exhibited by 20 were more modest, with TON of 5. The authors verified that the catalytic activity of the non-assembled components at the same concentrations is at a negligible level with TON of ca. 2 (20b, Table 1). Furthermore, the dependence of oxygen evolution rate on the catalyst concentration was studied for 20 and 20b (the assembly and equimolar mixture, respectively). While the multicomponent mixture **20b** exhibits saturation at $[20b]_0 > 60 \ \mu\text{M}$ (with the oxygen evolution rate of 1 $\mu\text{M s}^{-1}$ and TOF of 0.02 s^{-1} at $[20b]_0 = 60 \mu$ M), the assembly 20 shows linear increase of the reaction rate in the $10 < [20]_0 < 10^{-1}$ 100 μ M concentrations rate, exhibiting a constant TOF of 7 \times 10⁻³ s⁻¹. Monitoring of the reaction mixtures by UV-Vis spectroscopy disclosed a gradual decay of the absorption at 465 nm, attributed to the metal to ligand charge transfer (MLCT) band [10,32] of [Ru(bpy)₃]²⁺, dropping ca. twice after 60 min. However, the authors note that degradation of the photosensitizer is not a limiting factor because the oxygen evolution stops much earlier, within 30 min [61]. Since the decoordination of the carboxylic group was suggested to be a part of the water oxidation mechanism, the inactivation pathway may involve irreversible decoordination of the ligands L^7 and L^8 with following degradation of the supramolecular assembly.



Scheme 4. Schematic representation of assembly 21.



Figure 6. Accumulations of the oxygen in the course of water oxidation catalyzed by assemblies $\{Co_4O_4(OAc)_3(Py)_4\}\{(L^7)Ru(bpy)_2\}$ (**20a**, blue line) and $\{Co_4O_4(OAc)_2(Py)_4\}_2\{(L^8)Ru(bpy)_2\}_2$ (**21**, red line), as well as the equimolar mixture of $[Co_4O_4(OAc)_3(Py)_4]$ and $[Ru(bpy)_3]Cl_2$ (**20b**, black line). Complex $[Co_4O_4(OAc)_3(Py)_4]$ is equivalent to **9**. Adapted with permission from [61], Wiley, 2014.

4. Other Tetranuclear Complexes and Complexes of Higher Nuclearity

The polynuclear all-inorganic complex Na₁₀[Co₄(H₂O)₂(VW₉O₃₄)₂] (**22**) bearing polyoxometalate ligand (Figure 7) was tested as a catalyst for the water oxidation under chemical oxidation with [Ru(by)₃]³⁺ as well as the light-driven conditions [62]. Chemical oxidation revealed exceptionally high TOF values ranging from 1600 to 2200 s⁻¹ (adjusted for four cobalt centers in **22**), supported by TONs up to 75 (**22a**, Table 1). With such a high TOF the reaction completes within 1 s. In contrast, photocatalytic oxidation with in situ generated [Ru(bpy)₃]³⁺ revealed the lower TOFs of ca. 4 s⁻¹ (**22b**), but higher TON of 742 (or even up to 4210 for the lowest [**22**]₀, Table 1). The quantum efficiency of the catalytic system is at rather high level, up to 68% (for [**22**]₀ = 6 μ M). The integrity of the catalyst during the catalysis was monitored by means of UV-Vis and ⁵¹V NMR spectroscopes, which suggested no changes in the structure of **22**. The DLS experiments showed no presence of nanoparticles after both chemical and light-driven oxidations catalyzed by **22**. The comparative test using Co(NO₃)₂ as catalyst revealed formation of CoO_x nanoparticles with the radius of 220 nm [62].



Figure 7. Structure of the anion of the compound **22**. Color scheme: Co, pink; V, green; W, black; O, red; M–O–M bonds are highlighted by yellow.

Two coordination compounds $[Co_4(H_2O)_4(HL^9)_2(L^9)_2]$ and $K_{12}[Co(L^9)]_6$ (23 and 24, respectively) bearing tetra- and hexanuclear structures were prepared starting from N-(phosphonomethyl)iminodiacetic acid (H_4L^9) as pro-ligand (Figure 8) and cobalt chloride or acetate as a metal source, respectively [63,64]. Complex 23 disclosed TONs up to 662 (Table 1) in the

light-driven water oxidation. The standard set of experiments (UV-Vis and comparative DLS tests of **23** and cobalt nitrate pre-catalyst) were applied to confirm that no nanoparticles were formed after light-driven water oxidation using catalyst **23** [63]. Moreover, a set of extractions with following ICP–MS (inductively coupled plasma mass spectrometry) and CAdSV (catalytic adsorptive stripping voltammetry) experiments were performed, indicating that less than 0.35% of catalyst **23** released free Co^{2+} ions in the buffer solution. One may notice that cobalt nitrate, as pre-catalyst under the same conditions, showed TON of 150 (for $[Co^{2+}]_0 = 2 \mu M$). This value is even higher than that exhibited by catalyst **23** if adjusted for six cobalt atoms in its molecule (TON = 110).



Figure 8. Structure of complexes **23** and **24**. Color scheme: Co, pink; K, pale green; O, red; N, blue; P, pale pink. Structure **24** is presented in two views, without (left) and with (right) nearest potassium atoms.

The hexanuclear complex 24 features amongst the highest values of the TOF reported to date $(162.6 \text{ s}^{-1} \text{ per cobalt atom})$ for the light-driven water oxidation (Table 1) [64]. The use of perchlorate salt of the ruthenium photosensitizer is crucial since the chloride salt shows a ca. 4.7 times lower reaction rate (24a, Table 1). The maximum quantum efficiency was found to be 62.6%. Considering such a high parameters, it was important to establish the origin of the catalytically active species. The comparative test with $Co(OAc)_2$ revealed that the latter shows large lag period of 30 s at 5 μ M, while catalyst 24 shows no or negligible lag time. Furthermore, the chelation experiment using three equivalents of EDTA revealed no influence on the activity of 24, while the oxygen evolution catalyzed by cobalt acetate was ca. 50% suppressed (both catalysts were at 7 μ M initial concentration). The precipitate recovered after the reaction was studied by X-ray photoelectron spectroscopy (XPS) and was recognized as the authentic complex 24. The evidence reported by the authors looks convincing, although absence of the DLS experiment is an essential drawback of the investigation. The proposed mechanism of water oxidation involves participation of a single cobalt center only, what is in agreement with the first-order dependence of the reaction rate on the concentration of 24 (for $[24]_0 < 5 \mu M$) [64]. Kinetic isotope effect (KIE) k_H/k_D between parallel reactions in normal and deuterated water was found to be 2.53, suggesting that catalyst 24 acts via the WNA mechanism, where a dioxygen molecule

is constructed by the oxygen atoms from metal-oxo species and water molecule [7]. This value of KIE is very close to that reported (2.45) for ruthenium complex [Ru(bda)bpb]₃⁺ having cyclic structure (H₂bda = 2,2'-bipyridine-6,6'-dicarboxylic acid; bpb = 1,4-Bis(pyrid-3-yl)benzene) believed to operate via the WNA pathway [78]. Unfortunately, in the case of **24**, no ¹⁸O-labeling experiments were performed to confirm the attribution of the mechanism type.

The authors presented the structure of **24** as the open Co₆ ring (Figure 8, bottom-left) [62]. Such architecture could be rather labile in solution, especially under conditions of oxidative catalysis. Thus, the following questions appear: (1) Why is this compound is stable? (2) Why does it show such a high catalytic parameters? For instance, complex **23** is built using the same ligand (Figure 8) and does not possess water oxidation properties drastically different from those already reported (Table 1). The answer to both these questions could be found in the supramolecular structure of **24** (Figure 8, botom-right). The six-membered Co₆ ring is strengthened by potassium atoms, coordinating free oxygen atoms of the ligand, as well as numerous water molecules. Here, one may see two opportunities for the enhancement of the water oxidation reactions. At first, potassium may influence the redox potential of the cobalt centers, as it happens in the Ca₃Mn₄O₄ center of PSII and in the respective model complexes. Furthermore, recent experiments demonstrate that hydrogen bonding around the OEC in PSII is crucial for the water oxidation activity. The complex network of hydrogen bonds, formed by the water molecules coordinated by potassium atoms in the structure of **24**, may exist in a solution and be of great importance for successful water splitting process.

Another example of an all-inorganic compound of cobalt is the heptanuclear complex $Na_{12}[{Co^{II}}_{7}As_{6}O_{9}(OH)_{6}](SiW_{9}O_{34})_{2}]$ (25) [65]. The structure of 25 (Figure 9) resembles that of 22. In general, the catalytic activity of 25 in the water photocatalytic oxidation is in the range typically exhibited by the other cobalt complexes of lower nuclearity (Table 1). DLS measurements showed no nanoparticles after the light-driven reaction, while in comparative test with Co(NO_3)_{2} as catalyst, the presence of nanoparticles of ca. 190 nm in diameter were reported.



Figure 9. Structures of complexes 25–27, and 29 (for 25, 27, and 29 cationic counterions are omitted). Color scheme: Co, pink; W, black; As, dark red; Si, orange; Cl, green; O, red; N, blue.

The structure of the heptanuclear mixed-valence complex $[Co^{II}_5Co^{III}_2(mdea)_4(N_3)_2(CH_3CN)_6$ $(OH)_2(H_2O)_2](CIO_4)_4$ (**26**) $(H_2mdea = N-methyldiethanolamine) is based on the so-called Anderson structure type (Figure 9) [66]. Oxygen evolution was studied for chloride and perchlorate salts of ruthenium photosensitizer, showing that the latter produces higher TON values ($ **26b**and**26c**, respectively; Table 1). Using the chelating agents (bpy and EDTA), the decay of the oxygen evolution was observed when taken in equimolar ratio with the pre-catalyst**26**. The ESI-MS spectra indicated that**26**undergoes fragmentation in water solution since no peak attributable to Co₇ cluster was detected.

The octanuclear cobalt complex $K_8Na_8[Co_8(OH)_6(H_2O)_2(CO_3)_3SiW_9O_{34})_2]$ (27) containing bulky polyoxometalate ligand (the same as in 25) has been described [79] and studied [67] as catalyst for water oxidation. An interesting feature of the structure of 27 is the presence of carbonate ligands (Figure 9). Complex 27 acts as a catalyst for water oxidation, showing the highest efficiency at pH 9 with the highest TON of 1435 and highest TOF of 10 s⁻¹ (27b, Table 1). According to the DLS experiments, no nanoparticles are formed from 27 during the catalytic reaction. The comparative test with 2 μ M of Co(NO₃)₂ revealed nanoparticles with diameter of 78 nm. FT-IR and UV-Vis spectroscopes also evidenced that the complex keeps its integrity after the catalysis. ESI-MS data are also provided, but the spectra appear to be too noisy (low overall intensity) to use them to make definite conclusions.

A series of high-nuclear cobalt complexes with polyoxometalate capping ligands $K_{16}[Co_9(H_2O)_6 (OH)_3(PW_9O_{34})_3]$ (28) [80], $Na_5[Co_6(H_2O)_{30}\{Co_9Cl_2(OH)_3(H_2O)_9(SiW_8O_{31})_3\}]$ (29) [81] and $Na_{22}Rb_6[\{Co_4(OH)_3PO_4\}_4(PW_9O_{34})_4]$ (30) [82] have been recently tested as catalysts for light-driven water oxidation [68]. Compounds 28–30 obey rather complicated architectures (complex 29 is depicted at Figure 9 as an example). The electron transfer between complexes 28–30 and photogenerated $[Ru(bpy)_3]^{3+}$ has been studied in detail. No lag period has been detected in all cases. EXAFS and XANES experiments suggested the existence of water exchange processes with small alterations of the complexes cores, without their degradation. The catalytic parameters exhibited by 28–30 are modest with TONs not exceeding 105 (for $[29]_0 = 1.27 \mu$ M). In general, Complex 29 shows better performance among this series. The authors note that the structure of 29, containing 39 coordinated terminal water molecules, may facilitate its WOC activity [68].

5. Concluding Remarks

The field of the cobalt catalyzed water oxidation under visible light irradiation has received much attention in recent years. Pronounced activity of many molecular catalysts demonstrates great potential towards the construction of modular artificial water splitting systems. The TOF values exhibited by some of the catalytic systems approach those exhibited by the PSII system. However, one should always keep in mind that PSII and artificial systems operate at quite different conditions, thus any direct comparison of their parameters should be done with care. Furthermore, depending on the rate-limiting step of the catalytic reaction, the TOF may characterize, for instance, charge transfer between photosensitizer and catalyst, but not the rate of the dioxygen formation by the catalyst.

Discrimination of the true molecular (homogeneous) and heterogeneous systems should be always conducted to ensure that the molecular catalyst keeps its integrity and/or does not undergo heterogenization during the catalysis. The simplest methods involve comparative tests using cobalt salts with the same concentrations as that of the catalyst studied. Chelation experiments employing EDTA or bipyridine additives can provide fast evidence for the metal ions leaching. Purification of the sample from the metal impurities can also play an important role, as demonstrated by the examples of Co₄O₄ cubane complexes (**9–13**, Table 1). The typical instrumental method for nanoparticles detection is the dynamic light scattering (DLS), which is routinely applied in most of the literature reports discussed in the present review. However, one should remember that DLS has its own limitations and should not be used as a single method (see samples **7a** and **7b** as a representative example). Even the design of the experimental setup could have strong influence on the DLS results; for example, the use of magnetic stirring bars may complicate detection of nanoparticles possessing ferromagnetic properties.

Catalytic activity depends on many parameters, often implicit ones. For instance, the catalytic parameters exhibited by the systems containing $[Ru(bpy)_3](ClO_4)_2$ as photosensitizer are systematically higher than those obtained for using $[Ru(bpy)_3]Cl_2$. Thus, careful documentation of the experimental conditions is of exceptional significance for further analysis.

In spite of great efforts towards the study of the catalytic activity and verification of the catalyst stability, the reported reaction mechanisms are typically limited to general descriptions of charge transfers between photosensitizer and sacrificial electron acceptor, while attempts to study the mechanism of action of the WOC itself are scarce.

As a final remark, the use of cheap and abundant metals, such as cobalt, allows for the construction of highly efficient water oxidation catalysts. A special interest is in regards the bioinspired heterometallic complexes involving polynuclear cobalt core with attached redox-inactive metals. The exact mechanisms of many known artificial water oxidation systems are still unexplored and, beyond any doubt, further synthetic and catalytic efforts are required to establish structure-properties correlations towards practically feasible artificial photosynthesis.

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