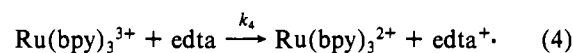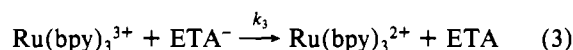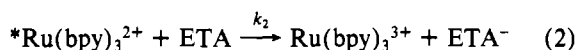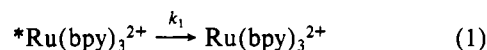# Communications

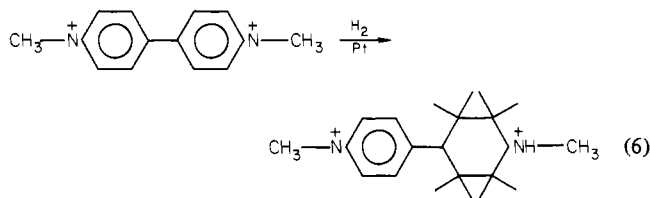## Cobalt Cage Complexes as Electron-Transfer Agents in the Photoreduction of Water

Sir:

We wish to communicate the properties of cobalt(III) cage complexes as electron-transfer agents (ETA) in the Ru-(2,2'-bipyridine)$_3^{2+}$ (Ru(bpy)$_3^{2+}$), Pt catalyst, ethylenediaminetetraacetic acid (edta) mediated photoreduction of water. This study identifies some complexes where the electron-transfer quenching is effective and others where energy-transfer quenching intervenes. The effective complexes are not quite as efficient as methylviologen for the production of hydrogen, but they have turnover numbers at least two orders of magnitude greater. The studies also point to a critical region of redox potential for the electron-transfer agent to achieve rapid H$_2$ production (i.e. ~0.3 V).

One of the most widely studied model systems for the photoreduction of water[1-22] consists of the excited state of *Ru(bpy)$_3^{2+}$, as a sensitizer, methylviologen (1,1'-dimethyl-4,4'-bipyridinium, mv^{2+}) as an electron-transfer agent, ethylenediaminetetraacetic acid as an electron donor, and platinum supported on polyvinyl alcohol (pva) as the electron-

transfer catalyst. Detailed studies have established that the initial rates of formation and yields of hydrogen are determined by reactions 1-5.[8,12,19-21]

$$*Ru(bpy)_3^{2+} \xrightarrow{k_1} Ru(bpy)_3^{2+} \qquad (1)$$

$$*Ru(bpy)_3^{2+} + ETA \xrightarrow{k_2} Ru(bpy)_3^{3+} + ETA^- \qquad (2)$$

$$Ru(bpy)_3^{3+} + ETA^- \xrightarrow{k_3} Ru(bpy)_3^{2+} + ETA \qquad (3)$$

$$Ru(bpy)_3^{3+} + edta \xrightarrow{k_4} Ru(bpy)_3^{2+} + edta^+ \cdot \qquad (4)$$

$$ETA^- + H^+ \underset{Pt/pva}{\rightleftharpoons} ETA + {}^1/_2 H_2 \qquad (5)$$

However, continuing irradiation leads to decreased evolution of hydrogen, which can cease even before the concentration of electron donor has become the limiting factor.[15-18] This decline is largely caused by reaction 6, which competes with

the formation of hydrogen and causes failure of the system by depleting the electron-transfer agent.[21] Besides reaction 6, mv^{2+} and its analogues are also degraded by a photochemical pathway involving *Ru(bpy)$_3^{2+}$ and mv$^+$.[22]

Colloidal platinum is widely used as a catalyst for the production of H$_2$ from mv$^+$· (reaction 5). Other metal catalysts are found to be less efficient. The aim of the current study is to investigate whether Co(III) cage complexes are efficient reagents to replace mv^{2+} in the above scheme.

The cage complexes used are derived from the ligands

sep[23]

sar[25]

azacapten[24]

oxosar-H[26]

(1) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Gleria, M. *Science (Washington, D.C.)* **1975**, *189*, 852.
(2) Schumacher, E. *Chimia* **1978**, *32*, 193.
(3) Bolton, J. R. *Science (Washington, D.C.)* **1978**, *202*, 705.
(4) Koriakin, B. V.; Dzhabiev, T. S.; Shilov, A. E. *Dokl. Akad. Nauk SSSR* **1977**, *233*, 620.
(5) Kirch, M.; Lehn, J. M.; Sauvage, J. P. *Helv. Chim. Acta* **1979**, *62*, 1345.
(6) DeLaive, P. J.; Sullivan, B. P.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 4007.
(7) Okura, I.; Kim-Thuan, N. *Chem. Lett.* **1980**, 1511.
(8) Kalyanasundaram, K.; Kiwi, J.; Grätzel, M. *Helv. Chim. Acta* **1978**, *61*, 2720.
(9) Harriman, A.; Porter, G.; Richoux, M.-C. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1939.
(10) Krasna, A. I. *Photochem. Photobiol.* **1980**, *31*, 75.
(11) Adams, M. W. W.; Rao, K. K.; Hall, D. O. *Photobiochem. Photobiophys.* **1979**, *1*, 33.
(12) Moradpour, A.; Amouyal, E.; Keller, P.; Kagan, H. *Nouv. J. Chim.* **1978**, *2*, 547.
(13) Kiwi, J.; Grätzel, M. *Nature (London)* **1979**, *281*, 657.
(14) Kiwi, J.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7214.
(15) Keller, P.; Moradpour, A. *J. Am. Chem. Soc.* **1980**, *102*, 7193.
(16) Keller, P.; Moradpour, A.; Amouyal, E.; Kagan, H. *J. Mol. Catal.* **1980**, *7*, 539.
(17) Keller, P.; Moradpour, A.; Amouyal, E.; Kagan, H. B. *Nouv. J. Chim.* **1980**, *4*, 377.
(18) Amouyal, E.; Grand, D.; Moradpour, A.; Keller, P., to be submitted for publication.
(19) Frank, A. J.; Stevenson, K. L. *J. Chem. Soc., Chem. Commun.* **1981**, 593.
(20) Miller, D.; McLendon, G. *Inorg. Chem.* **1981**, *20*, 950.
(21) Johansen, O.; Launikonis, A.; Loder, J. W.; Mau, A. W.-H., Sasse, W. H. F.; Swift, J. D.; Wells, D. *Aust. J. Chem.* **1981**, *34*, 981.
(22) Johansen, O.; Launikonis, A.; Loder, J. W.; Mau, A. W.-H.; Sasse, W. H. F.; Swift, J. D.; Wells, D. *Aust. J. Chem.* **1981**, *34*, 2347.
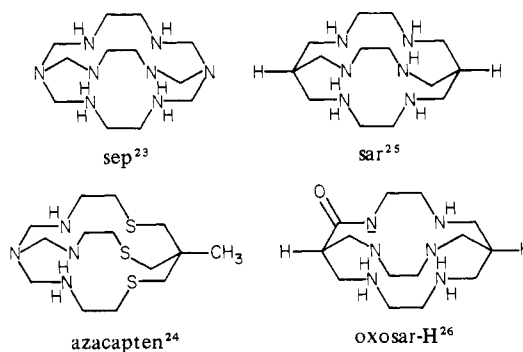
Table I. Hydrogen Production[a]

electron-transfer agent[a]	$E°$, V	rel rate of H_2 production	reacn mixture yield of H_2 (2 h irrad), μmol/mL	extra-polated turnover no.[21]
Co^{III}(meoxosar-H)$^{2+}$	−0.59	not detected	nil	
Co^{III}($COOC_2H_5$-meoxosar-H)$^{2+}$	−0.5	not detected	nil	
Co(sar)$^{3+}$	−0.42	4	0.9	
Co(NH$_2$mesar)$^{3+}$	−0.36	11	2.4	
Co(Clsar)$^{3+}$	−0.29	45	8.2	>5000[b]
Co(sep)$^{3+}$	−0.28	39	7.1	>5000[b]
Co(azacapten)$^{3+}$	−0.05	not detected	nil	
methylviologen(2+)	−0.44	100	19.6	55

[a] Conditions: solution containing electron transfer agent, 2×10^{-3} M; Ru(bpy)$_3{}^{2+}$, 6×10^{-5} M; edta, 2×10^{-2} M; Pt/pva with 5×10^{-5} M Pt with acetate buffer at pH 5 (0.15 M total acetate); 25 °C.[21] [b] This is a conservative estimate since the [Ru(bpy)$_3$]$^{2+}$ turnover number is ~10 000 under the conditions used. The HPLC estimation of the cage complex at the end of the reaction indicated no measurable (<5%) decomposition.
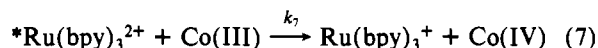
and an abbreviated nomenclature is used in the text to describe the substituents on the sar and oxosar ligands at the tertiary C caps. The oxosar ligand chelates as an anion through the amide N center.[26]

The rates of formation and yields of H_2 are listed in Table I arising from irradiation (Xe, 150 W) of an acetate buffer solution containing Ru(bpy)$_3{}^{2+}$, edta, a Co(III) cage complex, and Pt catalyst.[21] The data for the mv^{2+} experiments are included for comparison.

The rate of production and yield of H_2 obtained with Co-(Clsar)$^{3+}$ at pH 5 exceed those obtained with Co(sep)$^{3+}$. The use of Co(sep)$^{3+}$ as an ETA has already been reported,[27,28] and the rate of H_2 production observed here agrees with that in an earlier publication.[27] Three Co complexes gave no H_2 at all. Considering the similarity of the cages and the favorable redox potential, this was a surprising result. Accordingly, we have studied the excited-state quenching of *Ru(bpy)$_3{}^{2+}$ by these Co complexes in some detail. Linear Stern–Volmer plots (lifetime measurements) yield the bimolecular quenching constants, k_q, as listed in Table II. The excited-state reduction potential of *Ru(bpy)$_3{}^{2+}$, $E°$(Ru^{3+}/*Ru^{2+}) is −0.84 V.[8])

The quenching constants seem to bear no obvious correlation to the reduction potentials of these cobalt complexes. In particular, we note that k_q values for both of the Co(oxosar) complexes are higher than those of Co(sar)$^{3+}$ or Co-(NH$_2$mesar)$^{3+}$ (me = CH$_3$), although the latter complexes should be more easily reduced. Co(azacapten) stands out with k_q at least an order of magnitude higher than those of the rest of the Co complexes.
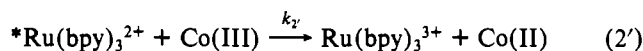
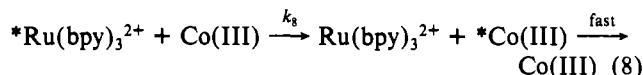Of possible quenching mechanisms, reductive quenching

$$*Ru(bpy)_3{}^{2+} + Co(III) \xrightarrow{k_7} Ru(bpy)_3{}^{+} + Co(IV) \quad (7)$$

can be ruled out because no metal-centered oxidation below

2 V has been observed[29] for the Co(III) complexes. Oxidative quenching

$$*Ru(bpy)_3{}^{2+} + Co(III) \xrightarrow{k_{2'}} Ru(bpy)_3{}^{3+} + Co(II) \quad (2')$$

and quenching by energy transfer

$$*Ru(bpy)_3{}^{2+} + Co(III) \xrightarrow{k_8} Ru(bpy)_3{}^{2+} + *Co(III) \xrightarrow{fast} Co(III) \quad (8)$$

remain to be considered. The absorption spectra of saturated amine Co(III) complexes indicate that their low-lying triplet states ($^3T_1$, $^3T_2$)[30] are below that of Ru(bpy)$_3{}^{2+}$. In order to see the relative efficiency of these two quenching paths (reaction 2' and reaction 8), we have determined the quantum yield of the formation of Co(II) ($\Phi_{Co(II)}$) by continuous irradiation of Ru(bpy)$_3{}^{2+}$ at 460 nm. Since Co(II) has no appreciable absorption near the 470–490-nm region,[23] probing the absorbance decrease of Co(III) (ϵ_{490} = 608 M^{-1} cm^{-1} for Co(azacapten)$^{3+}$, ϵ_{490} = 200 M^{-1} cm^{-1} for Co-(COOC$_2$H$_5$meoxosar-H)$^{2+}$, and $\epsilon_{470} \approx$ 100 M^{-1} cm^{-1} for all other Co complexes) gives $\Phi_{Co(II)}$ as listed in Table II. The fourth column in Table II lists the maximum yield of Co(II) if all of the quenching leads to Co(II) (based on reactions 1 and 2'). The drop in $\Phi_{Co(II)}$ is much steeper than the decrease of Φ_{max} as the reduction potentials of the Co(III) complexes become more negative. Despite a quenching constant of 1.0 $\times$ 10^8 M^{-1} s^{-1} no Co^{II} (oxosar) complexes could be detected even after prolonged irradiation. This is consistent with the result in Table I that no hydrogen formation was measured in these instances. Laser flash photolysis of a mixture containing Ru(bpy)$_3{}^{2+}$ and Co(sep)$^{3+}$ yields Co(II) and Ru-(bpy)$_3{}^{3+}$ in agreement with Houlding et al. and Scandola et al.[27,28] Attempts were made also to determine the percentage of formation of Ru(III) in this system. Excitation of Ru-(bpy)$_3{}^{2+}$ led to the enhanced light transmission at 470 nm due to the bleaching of ground-state Ru(bpy)$_3{}^{2+}$ and the absorption of *Ru(bpy)$_3{}^{2+}$ and Ru(bpy)$_3{}^{3+}$ generated by the flash.[27] We have used Fe^{3+} (5 $\times$ 10^{-3} M) for comparison since the quantum yield of Ru^{3+} formation is known to be near unity ($\Phi_{Ru(III)}$ = 0.9 ± 0.1).[31,32] On the basis of bleaching at 470 nm observed for the Ru(bpy)$_3{}^{3+}$/Fe^{2+} couple, $\Phi_{Ru(III)}$ is 0.6 for Co(azacapten) and 0.05 for Co(sep), confirming the $\Phi_{Co(II)}$ measured under continuous-irradiation experiments (Table II).

Formation of Ru(bpy)$_3{}^{3+}$ was not observed for either of the Co(oxosar) complexes. This indicates either energy transfer (reaction 8) or lack of charge separation (reaction 2') as the cause. Since electron transfer (2') is so efficient with Co-(azacapten)$^{3+}$ ($k_{2'} \approx k_q$, Table II) charge separation must be near unity. We suggest therefore that reaction 8 is the source of inefficient electron transfer for some of the cage complexes. It follows that where the electron-transfer path is slower the energy-transfer path is relatively more efficient. That correlation is observed in Table II provided the Hush–Marcus correlations hold, which they do with the cage complexes,[33] at least in the ground-state reactions.

The back-reaction k_3 for those Co(II) complexes where it is observed is estimated to be in the range (5 $\times$ 10^8)–(2 $\times$ 10^9) M^{-1} s^{-1} on the basis of the slower recovery of the 470-nm signal due to Ru(III) reverting to Ru(II) (300 μs for Co(azacapten)$^{2+}$ and 150 μs for Co(sep)$^{2+}$).

The lack of hydrogen formation from Co(azacapten)$^{3+}$ (Table I) despite a very high $\Phi_{Co(II)}$ (Table II) must be caused by its unfavorable potential (−0.05 V) to reduce water at pH

(23) Creaser, I. I.; Geue, R. J.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016 and references therein.
(24) Gahan, L. R.; Hambley, T. W.; Sargeson, A. M.; Snow, M. R. *Inorg. Chem.* **1982**, *21*, 2699.
(25) Harrowfield, J. M.; Sargeson, A. M., submitted for publication in *J. Am. Chem. Soc.*
(26) Petri, W. R.; Sargeson, A. M.; Snow, M. R., to be submitted for publication.
(27) Houlding, V.; Geiger, T.; Kölle, U.; Grätzel, M. *J. Chem. Soc., Chem. Commun.* **1982**, 681.
(28) Scandola, M. A. R.; Scandola, F.; Indelli, A.; Balzani, V. *Inorg. Chim. Acta* **1983**, *76*, L67.

(29) Lay, P. A. Ph.D. Thesis, The Australian National University, 1981.
(30) Wilson, R. B.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 4085.
(31) Lin, C.-T.; Sutin, N. *J. Phys. Chem.* **1976**, *80*, 97.
(32) Taylor, D. G.; Demas, J. N. *J. Chem. Phys.* **1979**, *71*, 1032.
(33) Creaser, I. I.; Sargeson, A. M.; Zanella, A. W. *Inorg. Chem.*, in press.

Table II. Quenching of *Ru(bpy)$^{3+}$ by Co(III) Cage Complexes

electron-transfer agent	$E°$, V^d	$10^{-8}k_q$,^{b} M^{-1} s^{-1} (acetate buffer, 0.5 M NaClO$_4$)	Φ_{max}^{c}	$\Phi_{Co(II)}$^{a,b}	$10^{-8}k_2'$, M^{-1} s^{-1}	k_2'/k_q
Co^{III}(meoxosar-H)$^{2+}$	−0.59	0.7 (2.8)	0.08	<10^{-4}	<10^{-3}	
Co^{III}(COOC$_2$H$_5$meoxosar-H)$^{2+}$	−0.53	1.0 (3.6)	0.11	<10^{-4}	<10^{-3}	
Co^{III}(sar)$^{3+}$	−0.42	0.4 (2.2)	0.05	4 × 10^{-3}	0.03	0.08
Co^{III}(NH$_2$mesar)$^{3+}$	−0.36	0.6 (3.3)	0.06	0.01	0.08	0.13
Co^{III}(Clsar)$^{3+}$	−0.29	1.3 (3.0)	0.14	0.05	0.42	0.32
Co^{III}(sep)$^{3+}$	−0.28	1.5 (2.2)^{27} (5.5)	0.15	0.04	0.34	0.23
Co^{III}(azacapten)$^{3+}$	−0.05	13.2 (58)	0.62	0.6	12.0	0.89

^{a} Same reaction mixture as Table I but in the absence of Pt. ^{b} k_q and the formation of Co(II), $\Phi_{Co(II)}$, are sensitive to the ionic strength of the solution. No attempt has been made to optimize the H$_2$ evolved by varying the ionic content. ^{c} Equal to $k_q[ETA]/(k_q[ETA] + k_1)$. ^{d} 0.1 M NaClO$_4$.
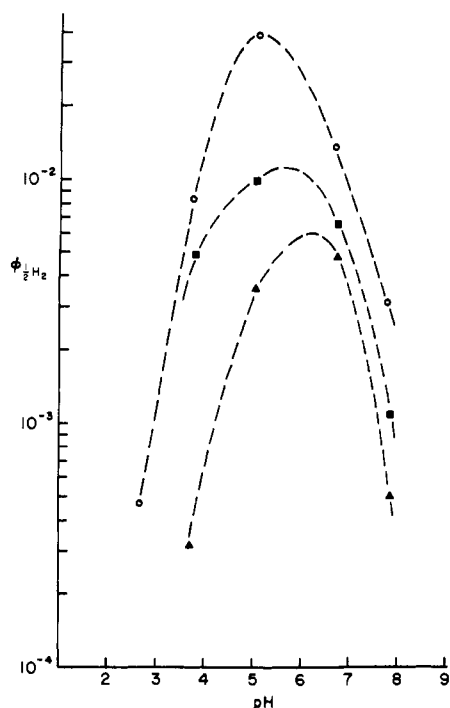

Figure 1. Quantum yield of hydrogen formation as a function of pH for the conditions given in Table I: (O) Co(sep)$^{3+}$; (■) Co-(NH$_2$mesar)$^{3+}$; (▲) Co(sar)$^{3+}$.

5. H$_2$ is formed quite readily if the reaction mixture (pH 5) is connected electrochemically to an acidic solution (pH 0) with Pt electrodes.

The quantum yield of hydrogen formation $\Phi_{1/2H_2}$ as a function of pH is plotted in Figure 1. The maximum rate is at pH 5 for Co(sep)$^{3+}$, whereas for Co(sar)$^{3+}$, it is near pH 6. Since $\Phi_{1/2H_2}$ (pH 5) is nearly equal to $\Phi_{Co(II)}$ (Table II), reaction 5 must be very efficient for these complexes.

If we consider the rate of hydrogen formation by using Pt as catalyst, mv^{2+} is a better electron-transfer agent than the Co(III) complexes (Table I). However, with other metal oxides the performance of mv^{2+} is worse. For example, if colloidal RuO$_2$ dispersed in silica (5 × 10^{-5} M Ru) is used as catalyst^{34,35} and the reaction mixture is normalized to 1-L volume, the rate of H$_2$ formation for Co(Clsar)$^{3+}$ is 55 μmol min^{-1} but with mv^{2+} the rate is only 11 μmol min^{-1} under identical experimental conditions. With RuO$_2$ as catalyst the driving force of mv$^+$· ($\Delta G \approx$ −0.14 V at pH 5) is insufficient to reduce water effectively and mv$^+$· accumulates in the re-

action mixture. Despite $\Delta G \approx$ +0.01 V (Co(Clsar))$^{2+}$ forms hydrogen quite readily.

Analysis by HPLC^{36} shows that the Co(II) cage complexes have turnover numbers for the formation of hydrogen at least two orders of magnitude higher than that of mv^{2+}, but aspects of the ease of electron transfer (k_2) and the degree of separation in this process need further investigation.

(36) Conditions as in ref 21 but eluent was an aqueous solution of THF (10%), CH$_3$COOH (1%), sodium heptasulfonate nonahydrate (0.08%), and methanesulfonic acid (0.02%), neutralized to pH 3.1 with tetramethylammonium hydroxide.

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Ionic Strength Dependence of the Volume of Activation for Reactions between Ions

Sir:

The study of inorganic substitution reactions through the measurement of volumes of activation has recently become an active field of research.^{1} Several research groups are now extending these studies to electron-transfer reactions.^{2} Since the molal volumes of ions are strongly dependent on solvent electrostriction, which in turn is influenced by the ionic strength of the medium,^{3} it is important to consider the influence of ionic strength on volumes of activation. This paper presents the expression for the dependence of the volume of activation on ionic strength, which is analogous to the typical

(34) Amouyal, E.; Keller, P.; Moradpour, A. *J. Chem. Soc., Chem. Commun.* **1980**, 1019.
(35) Prepared by depositing RuCl$_3$ (Fluka) on spherical SiO$_2$ particles (average diameter 40 Å) called Nalcoag 1115 from Nalco Chemical Co., Oak Brook, IL 60521.

(1) (a) Palmer, D. A.; Kelm, H. *Coord. Chem. Rev.* **1981**, *36*, 89. (b) Suvachittanont, S. *J. Chem. Educ.* **1983**, *60*, 150.
(2) (a) van Eldik, R. *Inorg. Chem.* **1983**, *22*, 353. (b) Ueno, F. B.; Sasaki, Y.; Ito, T.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1982**, 328. (c) Sasaki, Y.; Ueno, F. B.; Saito, K. *Ibid.* **1981**, 1135.
(3) Millero, F. J. *Chem. Rev.* **1971**, *71*, 147.