

Energy vs. electron transfer processes involving a novel cobalt cage complex

Christian Königstein,^{*a,b,c†} Albert W. H. Mau,^{*a‡} Peter Osvath,^{*a,b§} and Alan M. Sargeson^{*b¶}

^a Division of Chemicals and Polymers, CSIRO, Clayton, Victoria 3169, Australia

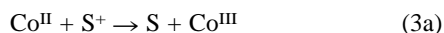
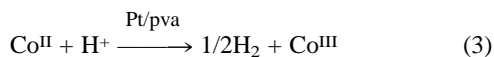
^b Research School of Chemistry, The Australian National University, Canberra ACT 0200, Australia

^c Institute of Physical Chemistry, Vienna University of Technology, Getreidemarkt 9/156, A-1060 Wien, Austria

A novel cage complex, [Co(Me₂-N₃S₃absar)]³⁺, able to undergo fast and efficient electron transfer reactions, is examined as an electron transfer agent in photocatalytic systems aimed at generating H₂; its electrochemical behaviour and excited state quenching properties are described.

The ability to capture energy and transfer it *via* redox reactions is a key issue in the photochemical conversion of solar energy. Artificial systems have used the viologens,^{1,2} polypyridinium complexes,³ or cobalt cage complexes^{4–6} as electron transfer agents. The high chemical stability of the cobalt cages allows the Co^{II}–Co^{III} redox states to be cycled repeatedly without decomposition. Systems using [Co(sep)]³⁺, [Co(sar)]³⁺ (Fig. 1) and their derivatives as electron relay compounds gave comparable rates of H₂ formation^{4–6} to those using methyl viologen (MV²⁺). Although their overall efficiency of conversion of light to hydrogen (Φ₃H₂) was only *ca.* 10%, their turnover numbers were at least three orders of magnitude higher than those of the viologens, and there is potential for improvement.

The rate of photoinduced H₂ formation is controlled by the generation of an excited state S* of the sensitiser (1), and three distinct electron transfer processes [eqns. (2), (3), (3a)].



Step (3) is essentially quantitative in the presence of the colloidal Pt/pva catalyst.⁴ The rate constants of the electron transfer processes are governed by the respective reduction potentials and the electron self-exchange rate constants of the reaction partners. As the driving force for eqn. (2) is reduced (*i.e.* the reduction potential of the cobalt complex becomes more negative), energy transfer from the excited state competes with electron transfer. On the other hand, a more negative reduction potential is desirable for H₂ evolution [eqn. (3)]. These conflicting demands need to be optimised.

The electron transfer rates of the CoN₆ cages are lower than that of MV²⁺, because of their lower self-exchange rates (k_{11} *ca.* 1–5 m⁻¹ s⁻¹),⁷ and this is a limiting factor in their use. The CoN₃S₃ cages however, have much higher self-exchange rate constants (k_{11} *ca.* 10⁴ m⁻¹ s⁻¹),^{8,9} but their cobalt(ii) complexes are weaker reductants than the CoN₆ cages (by *ca.* 350 mV) so

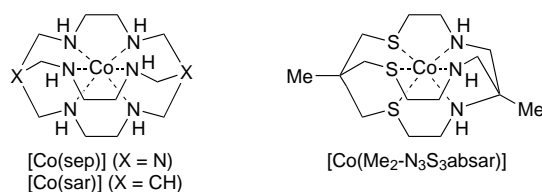


Fig. 1 Cobalt cage complexes

H₂ production is modest at pH ≤ 5.4.¹⁰ Synthetic efforts were therefore directed to the preparation of CoN₃S₃ cages with contracted cavities,¹⁰ as these should have a more negative reduction potential. Recent efforts to prepare [Co(Me₂-N₃S₃sar)]³⁺ led to a novel and efficient method of synthesising the contracted cavity cage [Co(Me₂-N₃S₃absar)]³⁺ ([CoL]³⁺, Fig. 1), in which a methylene unit is missing from the cap.¹¹ The smaller cavity, and the inductive effect of the apical methyl group lowered the reduction potential by *ca.* 200 mV compared with other CoN₃S₃ cages¹⁰ ($E = -0.20$ V vs. NHE, reversible one-electron process).¹¹ The cobalt(ii) complex should reduce protons in the presence of a colloidal platinum catalyst (at pH ≤ 3), and together with the high electron self-exchange rate ($k_{11} = 1.3 \times 10^4$ m⁻¹ s⁻¹),⁹ this made it a promising candidate for use as an electron transfer agent for light-induced H₂ formation.

Excited-state quenching reactions were studied with both [Ru(bpy)₃]²⁺ and anthracene carboxylate (AA⁻) as sensitisers. Earlier results with MV²⁺ had shown that AA⁻ had a much higher cage escape yield (Φ_{ce} = 1) than [Ru(bpy)₃]²⁺ (Φ_{ce} = 0.25).¹² The rate constants for energy and electron transfer involving the excited singlet and triplet states of AA⁻ with [CoL]³⁺ are shown in Fig. 2. Both the excited ¹AA⁻ and ³AA⁻ states were quenched by [CoL]³⁺ at pH = 7, but linear Stern–Volmer plots (indicating dynamic quenching) were obtained only for the ³AA⁻ quenching ([CoL]³⁺ ≤ 5 × 10⁻³ m).^{**} The non-linear Stern–Volmer plots obtained for ¹AA⁻ quenching imply some initial ground-state complex formation. This was also concluded from $k_q = 2 \times 10^{11}$ m⁻¹ s⁻¹ (obtained for low quencher concentrations where a degree of linearity was observed in the Stern–Volmer plots), which is higher than diffusion limited rate constants (*ca.* 10¹⁰ m⁻¹ s⁻¹). Both excited states are capable of reducing [CoL]³⁺ [Fig. 2, $E^\circ(^1\text{AA}^- - \text{AA}^-) = -2.2$ V vs. NHE, $E^\circ(^3\text{AA}^- - \text{AA}^-) = -0.88$ V].¹² However, with an energy of 2.67 eV for the ¹A₁ → ¹T₁ transition of [CoL]³⁺, energy transfer from ¹AA⁻ to Co^{III} is also possible.

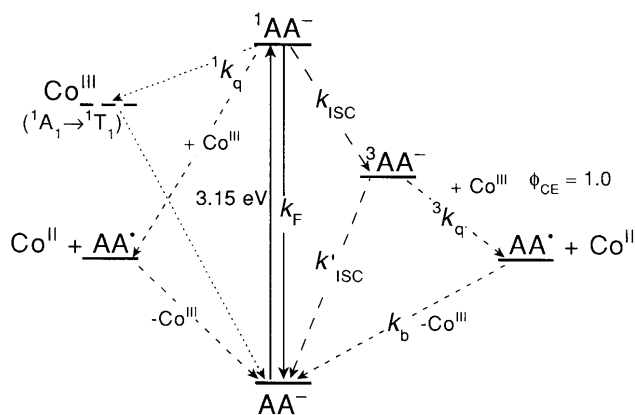


Fig. 2 Energy and electron transfer processes between AA⁻ and [CoL]³⁺. Radiative transitions (—), non-radiative transitions (---), electron transfer processes (- - - - -), energy transfer processes (.....). Co^{III} = [CoL]³⁺; Co^{II} = [CoL]²⁺.

$^3AA^-$ quenching to yield $[CoL]^{2+}$ occurs exclusively via excited-state electron transfer (efficiency ca. 100%, $k_q = 3 \times 10^9 \text{ m}^{-1} \text{ s}^{-1}$). The very high cage escape yield and the enhanced intensity of the $^1A_1 \rightarrow ^1T_1$ transition of $[CoL]^{3+}$ ($\lambda_{\text{max}} = 460 \text{ nm}$, $\epsilon = 640 \text{ m}^{-1} \text{ cm}^{-1}$) allowed us to measure for the first time the bleaching†† of the ground-state absorption of a cobalt(III) cage complex due to electron transfer (Fig. 3). The cage escape yield was determined to be close to unity, and interestingly, the rate constant for the back electron transfer ($k_b = 7 \times 10^8 \text{ m}^{-1} \text{ s}^{-1}$, Fig. 2) was smaller than that obtained with MV^{2+} ($k_b = 2.7 \times 10^9 \text{ m}^{-1} \text{ s}^{-1}$).¹² Thus, the overall quantum yield for the light-induced charge separation giving $[CoL]^{2+}$ and AA^\bullet is very high. Assuming a quencher concentration of $5 \times 10^{-4} \text{ m}$, 13% of the excited singlet state is deactivated via electron/energy transfer to $[CoL]^{3+}$, 6% is reemitted as fluorescence, and the yield of triplet formation is 81%. If only the triplet state participates effectively in the electron transfer to $[CoL]^{3+}$, 80% of the initially absorbed photons lead to the charge-separated state ($[CoL]^{2+} + AA^\bullet$). Steady-state photolysis experiments with $H_4\text{edta}$ as a sacrificial electron donor confirmed the quantum yield of $\eta = 0.8$ for the formation of $[CoL]^{2+}$. The main contribution to the electron transfer and charge separation is from the $^3AA^-$ state, whereas energy transfer predominates over electron transfer from $^1AA^-$, which is also the case for MV^{2+} .¹² Comparing the excitation energy (3.15 eV) with the energy of the products (1.13 eV) after charge separation, 36% of the excitation energy is stored (Fig. 2).

$[CoL]^{3+}$ excited-state electron transfer with $[Ru(\text{bpy})_3]^{2+}$ as photosensitiser ($k_q = 8.9 \times 10^8 \text{ m}^{-1} \text{ s}^{-1}$) has a comparable quenching rate constant to MV^{2+} ($k_q = 9.6 \times 10^8 \text{ m}^{-1} \text{ s}^{-1}$),⁴ but is higher than those for $\text{Co}^{\text{III}}\text{N}_6$ cages with similar reduction potentials ($[\text{Co}(\text{Cl}_2\text{-sar})]^{3+}$: $k_q = 2.2 \times 10^8 \text{ m}^{-1} \text{ s}^{-1}$, $[\text{Co}(\text{sep})]^{3+}$: $k_q = 1.4 \times 10^8 \text{ m}^{-1} \text{ s}^{-1}$),⁴ as expected on the basis of the higher self-exchange rates of the CoN_3S_3 cages.^{8,9}

Unfortunately, the back-electron transfer rate constant and the yield of electron transfer and charge separation could not be measured because of the overlap of the $[CoL]^{3+}$ and $[Ru(\text{bpy})_3]^{2+}$ absorptions at ca. 460 nm.

$[CoL]^{3+}$ was able to mediate the photoinduced H_2 formation at pH 5 (standard conditions with MV^{2+}) with $[Ru(\text{bpy})_3]^{2+}$ as photosensitiser‡‡ ($\eta = 0.004$) despite the relatively positive potential compared with that of $MV^{2+}-MV^+$ ($\eta = 0.1$; $E^\circ = -0.44 \text{ V}$). A similar complex with a potential of ca. -0.4 V should give very efficient conversion, and this is now being sought.

Although AA^- does not possess an absorption band in the visible region of the spectrum, as long as energy transfer processes to the $^3AA^-$ state take place, its favourable high cage

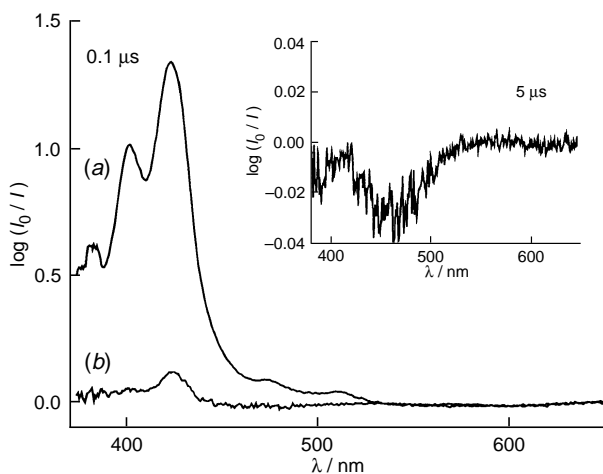


Fig. 3 Transient absorption spectra. (a) AA^- ($5 \times 10^{-4} \text{ m}$) in water; 100 ns after laser pulse (XeF_2 excimer, 50 mJ pulse^{-1}). (b) AA^- ($5 \times 10^{-4} \text{ m}$) + $[CoL]^{2+}$ ($3.33 \times 10^{-3} \text{ m}$); 100 ns after laser pulse. Insert: as (b) but $5 \mu\text{s}$ after laser pulse.

escape yield can be utilised. Energy transfer from the 3MLCT state of $[Ru(\text{bpy})_3]^{2+}$ to AA^- gives the $^3AA^-$ state in very high yield.¹³ More efficient storage of solar energy could thus be achieved using a series of molecules designed with the appropriate properties to optimise the efficiency of each step in the system. Antenna molecules which absorb a large part of the solar spectrum¹⁴ can be used to transfer light energy efficiently to anthracene. An assembly consisting of an antenna molecule, anthracene and a stable CoN_3S_3 cage of the type described here has the potential for efficient conversion of light energy to chemical energy.

C. K. thanks the 'Fonds zur Förderung der Wissenschaftlichen Forschung' (Project J0951-CHE) for financing his stay both at the ANU and at the CSIRO, Australia.

Footnotes

† E-mail: ckoenigs@fbch.tuwien.ac.at

‡ E-mail: a.mau@chem.csiro.au

§ E-mail: p.osvath@chem.csiro.au

¶ E-mail: sargeson@rsc.anu.edu.au

|| Cyclic voltammetry was performed in 1.0 M KCl (purged with N_2) using an EG & G Princeton Applied Research model 174 A polarographic analyser and a model 175 universal programmer, a platinum flag counter electrode, a Ag/AgCl reference electrode, and either a hanging mercury drop electrode (EG&G PAR model 303) or a F-doped SnO_2 covered glass sheet (TCO-glass, electrode area 1.5 cm^2) as working electrode. The concentration of $[CoL]^{3+}$ was $4 \times 10^{-3} \text{ m}$.

** Stern-Volmer plots of excited singlet state quenching were obtained using fluorescence emission, measured with a Perkin Elmer LS 50 luminescence spectrometer. The kinetics of quenching of $^3AA^-$ and 3MLCT of $[Ru(\text{bpy})_3]^{2+}$ were investigated by measuring the lifetime of the triplet-triplet absorption of anthracene at 425 nm, using a 150 W xenon lamp (analysing light), a Bausch & Lomb high-intensity monochromator ($1350 \text{ grooves mm}^{-1}$), and an AMI 9658b photomultiplier. Transient absorption spectra were obtained using an EG & G Princeton Applied Research Model 1460 optical multichannel analyser. As excitation light ($\lambda_{\text{exc}} = 351 \text{ nm}$), a Lambda Physik LPX 100 excimer laser was used (XeF_2).

†† $[CoL]^{2+}$ has a much weaker absorption at 465 nm ($\epsilon = 100 \text{ m}^{-1} \text{ cm}^{-1}$) and a weak band at 550 nm ($\epsilon = 80 \text{ m}^{-1} \text{ cm}^{-1}$).

‡‡ Buffered solutions (pH 5) containing $3.75 \times 10^{-4} \text{ m}$ $[Ru(\text{bpy})_3]^{2+}$ (ClO_4), $2 \times 10^{-3} \text{ m}$ electron transfer agent (MV^{2+} or $[CoL]^{3+}$), $5 \times 10^{-5} \text{ m}$ colloidal platinum catalyst (stabilised by polyvinyl alcohol), and $2 \times 10^{-2} \text{ m}$ $H_4\text{edta}$, were irradiated using a 150 W tungsten lamp. The amount of H_2 evolved was measured by GC as described in ref. 4.

References

- C. Königstein, *J. Photochem. Photobiol. A: Chem.*, 1995, **90**, 141.
- S. Hühnig and H. Berneth, *Top. Curr. Chem.*, 1980, **92**, 1.
- K. Kalyanasundaram, *Coord. Chem. Rev.*, 1982, **46**, 159.
- I. I. Creaser, L. R. Gahan, R. J. Geue, A. Launikonis, P. A. Lay, J. D. Lydon, M. G. McCarthy, A. W. H. Mau, A. M. Sargeson and W. H. F. Sasse, *Inorg. Chem.*, 1985, **24**, 2671.
- V. Houlding, T. Geiger, V. Kölle and M. Grätzel, *J. Chem. Soc., Chem. Commun.*, 1982, 681.
- M. A. R. Scandola, F. Scandola, A. Indelli and V. Balzani, *Inorg. Chim. Acta*, 1983, **76**, L67.
- I. I. Creaser, A. M. Sargeson and A. W. Zanella, *Inorg. Chem.*, 1983, **22**, 4022.
- P. Osvath, A. M. Sargeson, B. W. Skelton and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1991, 1036.
- P. Osvath, A. M. Sargeson and A. W. Zanella, 1996, unpublished results.
- P. A. Lay, J. Lydon, A. W.-H. Mau, P. Osvath, A. M. Sargeson and W. H. F. Sasse, *Aust. J. Chem.*, 1993, **46**, 641.
- P. Osvath, A. M. Sargeson, A. MacAuley, R. E. Mendelez, S. Subramanian, M. J. Zaworotko and L. M. Broge, to be submitted.
- O. Johansen, A. W. H. Mau and W. H. F. Sasse, *Chem. Phys. Lett.*, 1983, **94**, 107.
- O. Johansen, A. W. H. Mau and W. H. F. Sasse, *Chem. Phys. Lett.*, 1983, **94**, 113.
- A. W. H. Mau, O. Johansen and W. H. F. Sasse, *Photochem. Photobiol.*, 1985, **41**, 503.

Received, 4th December 1996; Com. 6/08199A