Oxidative quenching of excited-state tetrakis(μ-pyrophosphito)diplatinate(ii) tetraanion by iodine atom transfer from iodopentacyanocobaltate(iii)

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Iodopentacyanocobaltate(iii) oxidatively quenches excited state tetrakis(μ-pyrophosphito)diplatinate(ii) tetraanion *via* iodine atom transfer.

The bridged binuclear complex $[Pt_2(pop)_4]^{4-}$ (pop = $H_2P_2O_5{}^{2-}$) has attracted great interest due to its distinctive excited-state properties. The triplet excited state $^3A_{2u}$ {denoted as $[{}^*Pt_2(pop)_4]^{4-}$} is known to be a strong oxidant and reductant, and has biradical character.[1–3] Quenching studies have shown that the excited state can be quenched by energy transfer, electron transfer, or atom transfer mechanisms.[4] The latter mechanism has been observed for organic quenchers, such as RX, ROH (X = Cl, Br, I; R = alkyl, aryl),[5] but quenching by coordination complexes has invariably occurred *via* energy or electron transfer. During a detailed study[6] of salt effects on the quenching interaction between $[Pt_2(pop)_4]^{4-}$ and the anions $[Co(CN)_5X]^{3-}$ (X = I, Br, Cl, N_3), we saw evidence for atom transfer in the quenching of $[{}^*Pt_2(pop)_4]^{4-}$ by $[Co(CN)_5I]^{3-}$. The finding provides new insight into the deactivation of excited-state metal complexes and further illustrates the rich photochemistry of this platinum dimer.

In our initial approach, the lifetime of $[Pt_2(pop)_4]^{4-}$ in deaerated 0.500 m KCl–0.010 m $HClO_4$ solution was measured using a nitrogen laser, wavelength shifted† by a separate cell containing quinine sulfate to provide 370 nm, fast decay pulses to excite preferentially $[Pt_2(pop)_4]^{4-}$. The $[Co(CN)_5I]^{3-}$ quencher, dissolved in 0.500 m KCl–0.010 m $HClO_4$ solution, was delivered in μl aliquots from a microburette directly into the $[Pt_2(pop)_4]^{4-}$ solution. The high electrolyte concentration served to promote[6] the anion–anion interaction and the choice of chloride established a chloride–iodide competition required to demonstrate the occurrence of atom transfer. The second-order quenching rate constant k_q was calculated from the Stern–Volmer plot and was found to be 2.1×10^8 m^{-1} s^{-1} at 22.0 ± 0.1 °C for the above ionic strength.

When a deaerated solution of 2.9×10^{-5} m $K_4[Pt_2(pop)_4]$, 1.7×10^{-4} m of $K_3[Co(CN)_5I]$ and 0.500 m KCl–0.010 m $HClO_4$ was irradiated by a Hg lamp at 370 nm, the absorption bands at 370 and 262 nm were bleached, accompanied by the development of new bands at 328 and 438 nm (Fig. 1). Reaction terminated when the light source was removed, showing that a genuine photochemical reaction not a thermal or photocatalytic process occurs. The peaks diminished were those of reactant $[Pt_2(pop)_4]^{4-}$, λ_{max} (ε) = 369 nm (3.4×10^4 m^{-1} cm^{-1}), and quencher $[Co(CN)_5I]^{3-}$, λ_{max} (ε) = 262 nm (1.8×10^4 m^{-1} cm^{-1}), and the spectral changes showed that quencher and $[Pt_2(pop)_4]^{4-}$ reacted in a 2 : 1 molar ratio. The product peaks could be attributed to $[Pt_2(pop)_4I_2]^{4-}$. They appeared at 328 and 438 nm which compares well to literature results for $[Pt_2(pop)_4I_2]^{4-}$, λ_{max} (ε) = 331 nm (4×10^4 m^{-1} cm^{-1}) and 438 (1.7×10^4),[8] and had the correct ratio, experiment A_{328}/A_{438} = 2.2 (lit.[8] $\varepsilon_{331}/\varepsilon_{438}$ = 2.4). Moreover, the amount of product $[Pt_2(pop)_4I_2]^{4-}$ formed was equal to the amount of $[Pt_2(pop)_4]^{4-}$ consumed, $(\Delta A/\varepsilon)_{[Pt_2(pop)_4I_2]^{4-}}$: $(\Delta A/\varepsilon)_{[Pt_2(pop)_4]^{4-}}$ = 1.0 ± 0.1. It can be concluded that $[{}^*Pt_2(pop)_4]^{4-}$ is oxidatively quenched by $[Co(CN)_5I]^{3-}$ to form $[Pt_2(pop)_4I_2]^{4-}$. The quantum yield for this photooxidation was calculated to be 0.083 ± 0.002.

Formation of $[Pt_2(pop)_4I_2]^{4-}$ in 0.5 m chloride is most unlikely *via* oxidative electron transfer and halide ion scavenging of the resulting mixed-valence Pt dimer. The result suggests a mechanism involving direct I atom transfer from $[Co(CN)_5I]^{3-}$ to form $[Pt^{II}Pt^{III}(pop)_4I]^{4-}$ [eqn. (1)].

$$[{}^*Pt_2(pop)_4]^{4-} + [Co(CN)_5I]^{3-} \xrightarrow{k_{AT}} [Pt^{II}Pt^{III}(pop)_4I]^{4-} + [Co(CN)_5]^{3-} \qquad (1)$$

The mixed valence species $[Pt^{II}Pt^{III}(pop)_4I]^{4-}$ can then form the observed $[Pt_2(pop)_4I_2]^{4-}$ product either by disproportionation or by further reaction with $[Co(CN)_5I]^{3-}$. The species $[Co(CN)_5]^{3-}$ will quickly undergo acid-catalysed decomposition to give Co^{II}(aq) and HCN under our conditions.[9]

The above mechanistic ambiguity was resolved in our second approach, which also avoided possible mechanistic complications at the high chloride concentration needed for the competition study. A solution of 2×10^{-5} m $[Pt_2(pop)_4]^{4-}$ and 2×10^{-4} m $[Co(CN)_5I]^{3-}$ in nitrogen-degassed 0.01 m $HClO_4$–saturated $KClO_4$ solution was flash photolysed with a 25 mJ, 10 ns pulse at 355 nm with monitoring of the triplet $[Pt_2(pop)_4]^{4-}$ emission at 514 nm, its excited-state absorption at 460 nm (fast), the $[Co(CN)_5I]^{3-}$ ground-state absorption at 280 nm and the development of $[Pt_2(pop)_4I_2]^{4-}$ product absorption at 460 nm (slow). The absorption and emission from the triplet excited state decayed exponentially with the quenched lifetime, 4.9 and 5.1 μs respectively, while the ground-state absorption of $[Co(CN)_5I]^{3-}$ decreased with the same lifetime (4.7 μs), Fig. 2(*a*). This proves the direct reaction of $[Pt_2(pop)_4]^{4-}$ triplet state with $[Co(CN)_5I]^{3-}$ consistent with eqn. (1). The transient

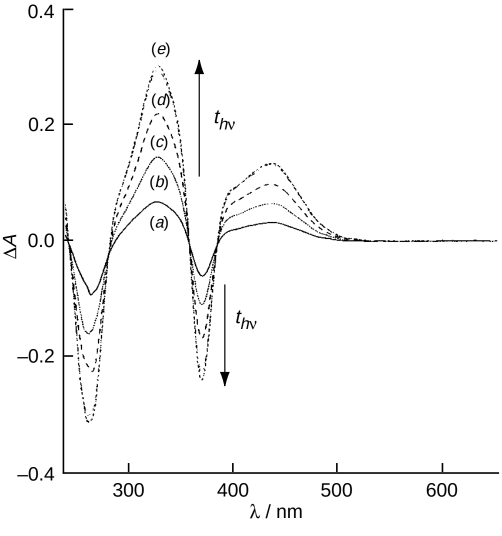

Fig. 1 Absorbance change with the reaction of $[{}^*Pt_2(pop)_4]^{4-}$ by $[Co(CN)_5I]^{3-}$ in 0.50 m KCl–0.010 m $HClO_4$ solution. Irradiation time: (*a*) 30, (*b*) 60, (*c*) 90, (*d*) 120 s; (*e*) kept in dark for 120 s after (*d*).

that results leads to $[Pt_2(pop)_4I_2]^{4-}$ which grows in with a 0.5 ms lifetime (see below), but no further reaction of $[Co(CN)_5I]^{3-}$ occurs (monitored at 280 nm) as shown in Fig. 2(*b*). This proves that the dominant second step of the reaction is a disproportionation process [eqn. (2)].

$$2[Pt^{II}Pt^{III}(pop)_4I]^{4-} \longrightarrow [Pt_2(pop)_4I_2]^{4-} + [Pt_2(pop)_4]^{4-} \qquad (2)$$

not further reaction with $[Co(CN)_5I]^{3-}$ such as a second atom transfer [eqn. (3)].

$$[Pt^{II}Pt^{III}(pop)_4I]^{4-} + [Co(CN)_5I]^{3-} \xrightarrow{k_{AT}} [Pt_2(pop)_4I_2]^{4-} + [Co(CN)_5]^{3-} \qquad (3)$$

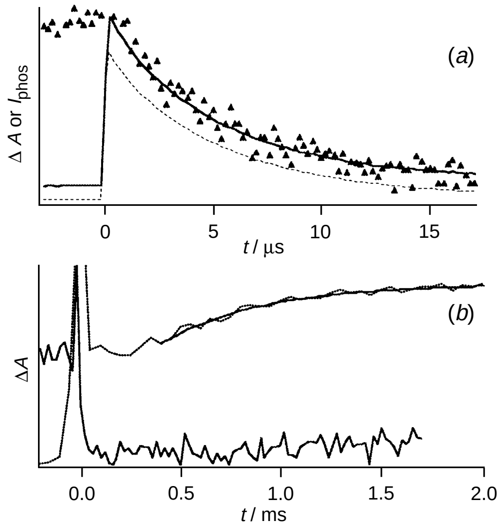

Fig. 2 Transient signals on flash photolysis of 2×10^{-5} m $[Pt_2(pop)_4]^{4-}$ and 2×10^{-4} m $[Co(CN)_5I]^{3-}$ in nitrogen-degassed 0.01 m $HClO_4$–saturated $KClO_4$ solution with a 25 mJ, 10 ns pulse at 355 nm. (*a*) (---) $[{}^*Pt_2(pop)_4]^{4-}$ emission at 514 nm; (—) $[{}^*Pt_2(pop)_4]^{4-}$ absorption at 460 nm; (▲) $[Co(CN)_5I]^{3-}$ absorption at 280 nm. (*b*) (—) $[Co(CN)_5I]^{3-}$ absorption at 280 nm; (···) $[Pt_2(pop)_4I_2]^{4-}$ absorption at 460 nm.

The disproportionation step should be simple second order, but given the noise level of the data, Fig. 2(*b*), the time evolution is indistinguishable from an exponential decay with a lifetime of 0.5 ms for these conditions.

In conclusion, both approaches show that direct iodine atom abstraction occurs in this system. A full paper with results on the salt and specific ion effects in the quenching of $[{}^*Pt_2(pop)_4]^{4-}$ by $[Co(CN)_5I]^{3-}$ and other pentacyanocobaltate complexes has been submitted.[6]

Footnote

† At 337 nm $[Pt_2(pop)_4]^{4-}$ has a much smaller molar absorptivity than $[Co(CN)_5I]^{3-}$. To quench the lifetime of $[Pt_2(pop)_4]^{4-}$ to half of its initial value, the quencher concentration should be about 10^{-3} m, while the concentration of $[Pt_2(pop)_4]^{4-}$ should be about 3×10^{-4} m to achieve an absorbance of 0.3 at 337 nm. Under such conditions the iodo complex would absorb 90% of the light, possibly leading to the photolysis of the quencher, as well as serious inner filter effects in the Stern–Volmer study. Quinine sulfate has a strong absorption between 320 nm and 340 nm (log ε = 4) and emits at 370 nm, where $\varepsilon\{[Pt_2(pop)_4]^{4-}\} \gg \varepsilon\{[Co(CN)_5I]^{3-}\}$, and has[7] a fluorescence lifetime of 19.2 ns, short enough to avoid distortion of the 9 µs emission decay curve of $[{}^*Pt_2(pop)_4]^{4-}$.

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