

Nuclear and Electronic Contributions to the Photoreactivity of Iso- and Hetero-polyoxomolybdates †

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Ligand-radical intermediates were detected in flash photolysis of the hexa- and octa-molybdates. The transients exhibited absorption spectra with maxima near 460 nm and lifetimes shorter than 1 ns. The photochemical transformations of these complexes are similar to those of the heptamolybdate and heteropolyoxomolybdates. The effect of the molecular structure on the electronic levels of iso- and hetero-polyoxomolybdates was investigated with an extended-Hückel method in order to rationalize their photochemical behaviour.

The polyoxomolybdates exhibit broad variations in nuclear and electronic structures which make them malleable substrates for photochemical studies.¹⁻¹¹ Numerous articles about their behaviour in the photodehydrogenation of organic compounds have been reported.⁴⁻¹⁰ Many of these reports were concerned with different applications of this family of compounds to photocatalysis.⁶⁻⁹ Other mechanistic studies have dwelled upon the role of the charge-transfer (c.t.) excited states and the ligand-radical polymolybdate intermediates I, in the early events of these photochemical reactions (Scheme 1).^{4,5,8-11}

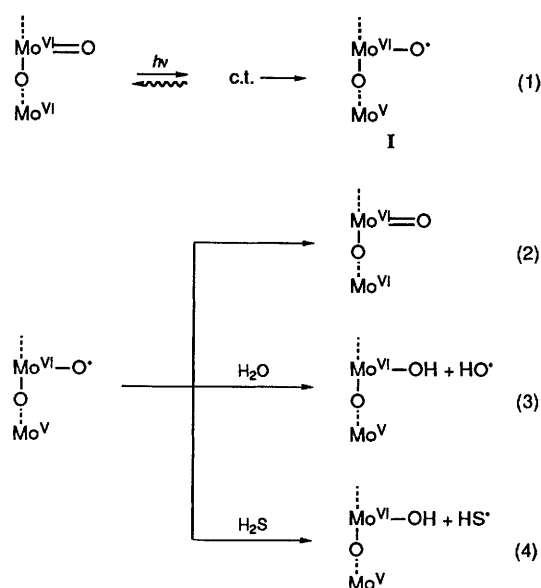
In our previous work we have investigated the effect of heterometallo ions and various nuclear structures on the photochemistry of the polymolybdates.^{4,5} These studies are complemented here with experimental observations on the photoreactivity of $[\text{Mo}_6\text{O}_{19}]^{2-}$ and $[\text{Mo}_6\text{O}_{19}]^{2-}$ and a comparison of their photochemical properties with those of related heteropolyoxomolybdates.

Experimental

Photochemical Procedures.—The flash-photolysis apparatus used for the measurements of spectra and reaction kinetics in the pico- and nano-second time domains, respectively, has been described elsewhere.^{4,12} In these experiments 355 or 266 nm pulses with width *ca.* 18 ps from a mode-locked YAG laser were used for the investigation of transients in a time range from 18 ps to 20 ns, while observations in the range 10 ns to 20 μ s were carried out in another flash-photolysis apparatus with an excimer laser or a YAG laser used as excitation sources.¹² Solutions of the polymolybdates were deaerated with streams of ultrapure N_2 .

Theoretical Calculations.—The semiempirical molecular orbital (MO) calculations used in this work have been described elsewhere.¹³⁻¹⁵ The extended-Hückel calculations were carried out with a modified Forticon program, QCPE Program No. 344, which allowed treatment of polyatomic molecules as large as octomolybdate. Contour plots of the point probability, $|\psi|^2$, were calculated for several contour levels of a molecular orbital, ψ . The MO orbitals were expressed as polynomials where each term was a product of a given Slater-type atomic orbital and the corresponding coefficient in the output of Forticon.

Materials.—The $[\text{NBu}_4]_2[\text{Mo}_6\text{O}_{19}]$, α - $[\text{NBu}_4]_3\text{K}[\text{Mo}_8\text{O}_{26}]$, β - $\text{K}_4[\text{Mo}_8\text{O}_{26}]$, β - $[\text{NH}_4]_4[\text{Mo}_8\text{O}_{26}]$ and β - $[\text{NBu}_4]_4[\text{Mo}_8\text{O}_{26}]$ ¹⁶⁻¹⁸ complexes were prepared and purified according to literature procedures. Other materials were reagent grade and used without further purification.



Results

Photochemical Experiments.—The ultraviolet photochemistries of $[\text{Mo}_6\text{O}_{19}]^{2-}$ and α - and β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ have been investigated in deaerated MeCN where these polyoxomolybdates exhibit considerable thermal stability.[‡]^{2,16-20} The equilibrium between the isomers of the octapolyoxomolybdate was shifted towards the α - $[\text{Mo}_8\text{O}_{26}]^{4-}$ by addition of NBu_4ClO_4 or towards β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ by the addition of NMe_4ClO_4 to their respective solutions.¹⁹ In MeCN a transient spectrum, $\lambda_{\text{max}} \approx 460$ nm and $t_3 \approx 5$ ns, has been generated in 308 nm flash irradiations of β - $[\text{Mo}_8\text{O}_{26}]^{4-}$, Fig. 1. The decay of the transient is not complete and additional measurements of the

† Non-SI unit employed: eV $\approx 1.60 \times 10^{-19}$ J.

‡ Studies about the structure of these compounds,¹⁶⁻²¹ have shown that the ions $[\text{Mo}_6\text{O}_{19}]^{2-}$, α - $[\text{Mo}_8\text{O}_{26}]^{4-}$ and β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ retain their solid-state structures in acetonitrile. The equilibrium between the α and β isomers of the octapolyoxomolybdate is respectively shifted towards one or the other by NBu_4^+ and K^+ .¹⁸ In photochemical experiments, the concentrations of the polymolybdates and the ionic strength were adjusted in order to displace the equilibria towards a given species. Only one isomer was photolysed under such experimental conditions.

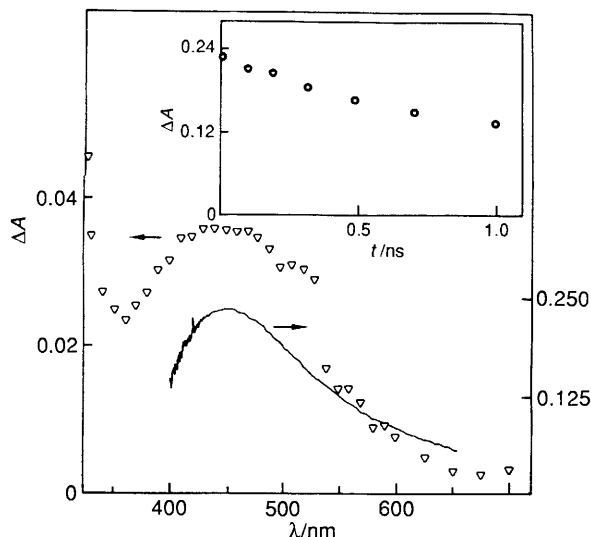


Fig. 1 Transient spectra observed 10 ps (solid line) and 20 ns after the 266 nm flash irradiation of 5.0×10^{-4} mol dm^{-3} β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ in deaerated MeCN. The spectra were recorded with 1.0 cm (solid line) and 0.2 cm (∇) optical paths. The insert shows the decay of the 460 nm optical density in a ps–ns time domain

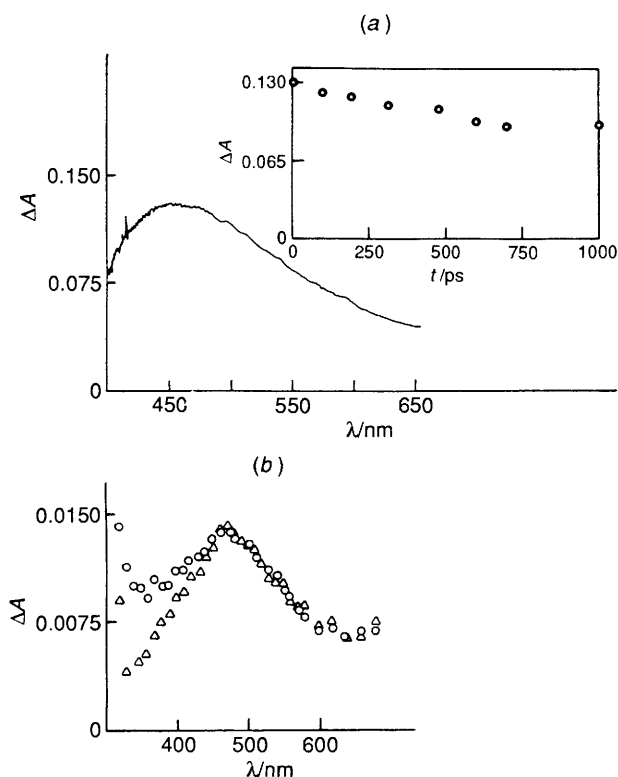


Fig. 2 Spectral changes observed after 266 nm flash irradiations of 5.0×10^{-4} mol dm^{-3} α - $[\text{Mo}_8\text{O}_{26}]^{4-}$ (ionic strength adjusted to 0.1 mol dm^{-3} NBu_4ClO_4) in deaerated MeCN. The spectrum recorded 10 ps after the irradiation is shown in (a) together with the time-resolved 460 nm optical density changes (insert). Spectral changes recorded respectively at 10 (∇) and 400 ns (\circ) after the irradiation are shown in (b)

optical density in a ns–ms time domain revealed spectral changes which are similar to those previously reported for other polymolybdates.^{4,5} It should also be noted that such spectral changes, observed at times longer than 1 μs , have been related earlier^{4,5} to chemical reactions leading to the formation of polyoxoblues. The photochemistry of β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ has also been investigated in aqueous solutions of the potassium salt where this molybdate is also thermally stable.¹ Flash

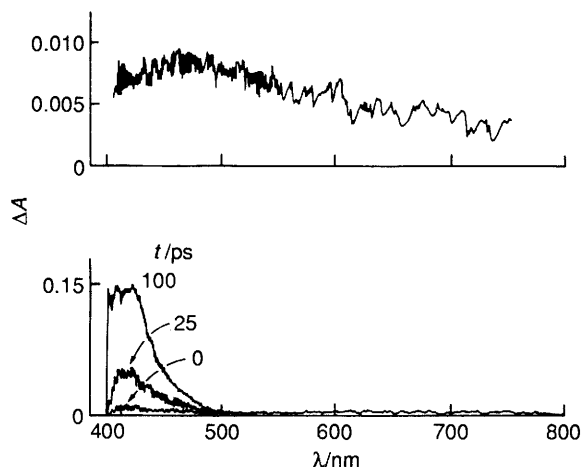


Fig. 3 Flash photolysis of 5.0×10^{-4} mol dm^{-3} $[\text{Mo}_6\text{O}_{19}]^{2-}$ in deaerated MeCN. Top: spectrum recorded 10 ps after excitation at 355 nm. Bottom: spectra recorded with various delays after the 266 nm irradiation

irradiations ($\lambda_{\text{exc}} = 266$ or 308 nm respectively) in millimolar aqueous deaerated solutions (pH 4 or 3) of the β isomer generate an intermediate ($\lambda_{\text{max}} \approx 450$ nm and $t_{\frac{1}{2}} \approx 15$ ns) which has been assigned as a ligand-radical polymolybdate by comparison with related species.^{4,5}

The lifetimes determined for the reaction intermediates generated in 308 nm flash irradiations of α - $[\text{Mo}_8\text{O}_{26}]^{4-}$ are slightly different from those measured with the β isomer. Indeed, the shortest lived species has a decay lifetime of 300 ps and it transforms into an unstable product whose lifetime is $t_{\frac{1}{2}} \approx 440$ ns, Fig. 2.

Irradiations at 266 and 355 nm of $[\text{Mo}_6\text{O}_{19}]^{2-}$ give rise to different optical transients, Fig. 3. Indeed, photolysis of the hexamolybdate at 266 nm generates a species, $\lambda_{\text{max}} \approx 425$ nm, with $t_{\frac{1}{2}} \approx 50$ ps. This short-lived product disappears with $t_{\frac{1}{2}} \approx 400$ ps. Photolyses at $\lambda_{\text{exc}} \approx 365$ nm generate the characteristic ligand-radical polymolybdate I,^{4,5} with $\lambda_{\text{max}} = 460$ nm and a yield between one and two orders of magnitude smaller than those from $[\text{Mo}_7\text{O}_{24}]^{6-}$ or $[\text{Mo}_8\text{O}_{26}]^{4-}$ under similar experimental conditions, i.e. $\phi \leq 10^{-2}$.

The small yields associated with UV photolyses of $[\text{Mo}_6\text{O}_{19}]^{2-}$ prevent an unambiguous determination of the species acting as an hydrogen donor in the photoreduction of the hexamolybdate. This is not the case with octamolybdates where product yields, namely $\phi_{\text{MeCN}}/\phi_{\text{NBu}_4^+} \approx 2.9 \times 10^{-2}$, have shown that the photooxidation of the solvent, ϕ_{MeCN} , is a minor event by comparison to the photooxidation of the counter ion, $\phi_{\text{NBu}_4^+}$.

Molecular Orbital Calculations.—In MO calculations of the $[\text{Mo}_6\text{O}_{19}]^{2-}$, $[\text{Mo}_7\text{O}_{24}]^{6-}$ and $[\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{n-}$ ($\text{M} = \text{Al}$, $n = 3$; Cr , 3; Ni , $n = 4$) electronic levels we have used bond distances reported in the literature for given polymolybdate crystallographic structures.^{1,22–24} Such calculations were optimized by charge iterations and Madelung potentials.¹⁵ The optimizations gave energies for the one-electron levels in accord with electronic transitions in the spectra of the complexes. The energies of the electronic levels involved in metal-centred, d–d and ligand-to-metal charge-transfer (l.m.c.t.) transitions are shown in Fig. 4. The energy of partially filled d shells in the heterometallo ions and the nuclear structure of the polymolybdate are factors that determine the extent of overlap between electronic clouds of closely placed ions, Figs. 5 and 6. Moreover, the highest occupied molecular orbital (HOMO) is delocalized over a limited number of oxide ions whose positions depend on the nuclear structure of the polymolybdate. For example, our calculations on the $[\text{HMo}_7\text{O}_{24}]^{6-}$ show a localization of electronic charge in accordance with literature reports on the

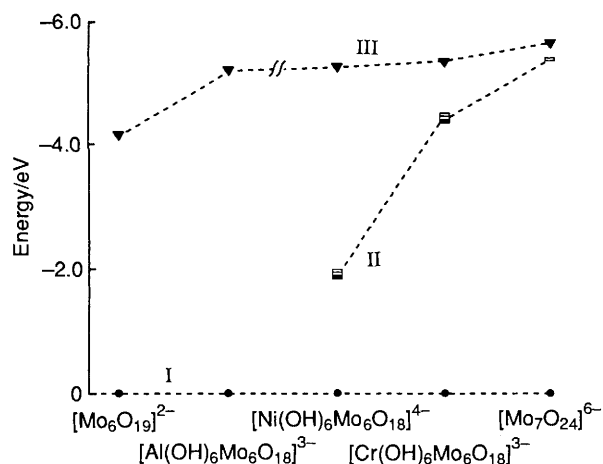


Fig. 4 Differences between one-electron energies of molecular orbitals in polyoxomolybdates. Energies of the orbitals II and III are given by reference to the energy of the ligand-centred HOMO I. Partially filled or empty molecular orbitals, II, receive large contributions from the d orbitals of hetero ions, namely Ni, Cr, or the centre Mo in $[\text{Mo}_7\text{O}_{24}]^{6-}$. The empty molecular orbital III is delocalized on equivalent molybdenum ions. Contour curves of the orbitals can be seen in Figs. 5 and 6

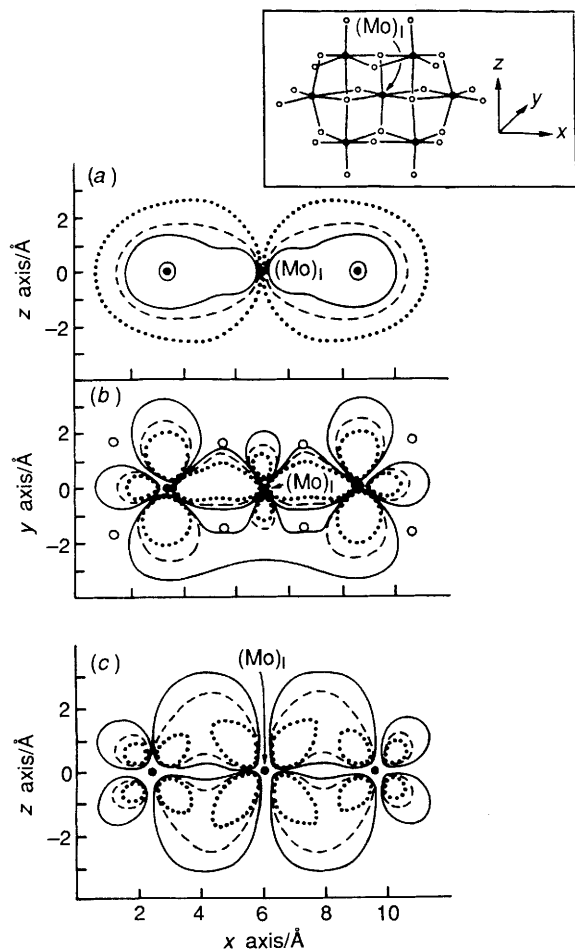


Fig. 5 Plots of the contour curves for the point probability, $|\psi|^2$, of a given molecular orbital ψ in $[\text{Mo}_7\text{O}_{24}]^{6-}$. Contours for 0.126 (dotted line), 0.084 (dashed line) and 0.042 (solid line) are shown in (a) for the second unoccupied orbital (III in Fig. 4). Curves shown in (b) and (c) correspond to the lowest unoccupied molecular orbital (II in Fig. 4). Note also that curves are on the coordinates plane xz in (a), xy in (b) and xz in (c). Solid and open circles respectively represent molybdenum(vi) and O^{2-} ions whose positions are shown in the insert. $(\text{Mo})_1$ is the central MO^{IV} ion

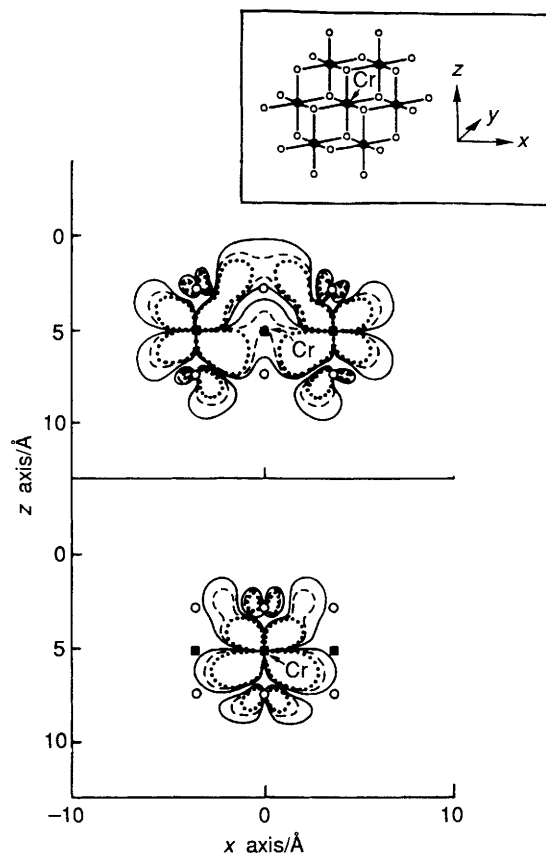


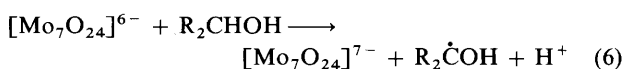
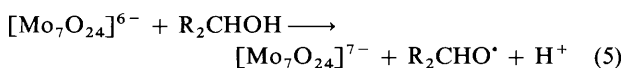
Fig. 6 Plots of the contour curves for the point probability, $|\psi|^2$, of a given molecular orbital ψ in $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$. The contours for 0.042 (dotted line), 0.028 (dashed line) and 0.014 (solid line) are given for the orbitals II (bottom) and III (top) described in Fig. 4. The insert shows the oriented structure of the heteropolymolybdate. Key: (■), Cr; (●), Mo; (○), O^{2-}

ESR spectrum of this species.²⁵ Charge-transfer transitions must be effective, therefore, in reducing the electron density of specific oxide ions, while nuclear and solvent reorganizations could stabilize polymolybdates with a ligand-radical structure.⁵ It should also be noted that in each compound there are quasi-degenerate levels. For example, a number of configurations involving orbitals with energies between 8.90 and 9.18 and between 9.36 and 9.74 eV can be respectively used in the description of the l.m.c.t. transitions of $\lambda_{\text{max}} \approx 210$ and 230 nm in the spectrum of $[\text{Mo}_7\text{O}_{24}]^{6-}$.²⁶ Since the electronic transitions from the ligand-localized HOMO to each of the Mo-localized orbitals must have similar values of the transition dipole,²⁶ the ratio of the levels density at the respective wavelengths, $\delta_{210}/\delta_{230} = 1.5:1$, is almost the same as the ratio of the corresponding absorption coefficients, $\epsilon_{210}/\epsilon_{230} = 1.6:1$. The order of electronic levels in $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ was qualitatively similar to that found for $[\text{Mo}_7\text{O}_{24}]^{6-}$.

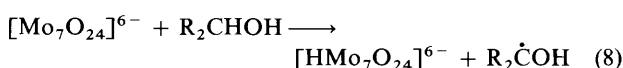
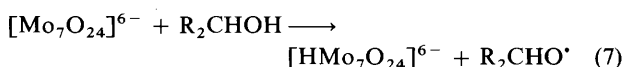
Discussion

Based on literature reports about the photochemical behaviour of $[\text{Mo}_7\text{O}_{24}]^{6-}$ and related heteropolymolybdates,^{4,5} the experimental observations reported above for $[\text{Mo}_6\text{O}_{19}]^{2-}$ and the isomers of $[\text{Mo}_8\text{O}_{26}]^{4-}$ can be rationalized in terms of a mechanism similar to the one described by Scheme 1. Moreover, the transient spectra and lifetimes measured for excitations of $[\text{Mo}_6\text{O}_{19}]^{2-}$ at 266 and 355 nm show that the intermediates I generated at these wavelengths must have some structural differences but a similar reactivity. The formation lifetime, $t_{\frac{1}{2}} \approx 50$ ps, suggests that the species is a ligand-radical polymolybdate formed by decay from an upper c.t. state. In this regard, the possibility of reduction of the polymolybdate by

electron or hydrogen donation from an organic substrate must be considered first from the standpoint of the reaction energetics. The appropriate combination of bond and ground-state energies calculated for each of the polymolybdates reveals that the one-electron reductions (5) and (6) are largely



endoergonic, $\Delta E > 800 \text{ kJ mol}^{-1}$, and that they would still be endoergonic if they were initiated from l.m.c.t. excited states of $[\text{Mo}_7\text{O}_{24}]^{6-}$ or from the ligand-radical species I. Hydrogen abstractions (7) and (8) are, however, slightly endoergonic or



exoergonic reactions, $14 > \Delta E > -26 \text{ kJ mol}^{-1}$, and would be considerably exoergonic, $\Delta E < -300 \text{ kJ mol}^{-1}$, if they involved the l.m.c.t. excited state or the corresponding ligand-radical species. Based on such thermochemical considerations, it is concluded that photocatalysed dehydrogenations, as shown in Scheme 1, should be regarded as hydrogen abstractions rather than electron transfers from organic substrates. The yields of the photoprocesses are, in this mechanism, the product of the quantum yield $\varphi_{\text{e.t.}}$ for the formation of the reactive state times the efficiency ξ of conversion of the excited state into the reactive ligand-radical polymolybdate. Variations of these two factors must be considered in order to account for a reactivity train, $[\text{Mo}_8\text{O}_{26}]^{4-} \approx [\text{Mo}_7\text{O}_{24}]^{6-} \approx [\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-} > [\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{n-}$ ($\text{M} = \text{Cr}^{\text{III}}, \text{Rh}^{\text{III}}, \text{Fe}^{\text{III}}$ with $n = 3$; Ni^{II} with $n = 4$) $> [\text{Mo}_6\text{O}_{19}]^{2-}$.* In the most photoreactive species of the series, $[\text{Mo}_8\text{O}_{26}]^{4-}$, $[\text{Mo}_7\text{O}_{24}]^{6-}$ and $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$, the lowest-lying excited state is ($\text{O}^{2-} \longrightarrow \text{Mo}^{\text{VI}}$) l.m.c.t. The lowest unoccupied molecular orbital (LUMO) populated in these transitions is localized in only two or three molybdenum ions and receives insignificant contributions from orbitals centred on the oxide ligands. This is not the case in $[\text{Mo}_6\text{O}_{19}]^{2-}$ where the LUMO is delocalized over the six molybdenum(vi) ions and over some bridging oxide ions. Although the distribution of charge in $[\text{Mo}_6\text{O}_{19}]^{2-}$ must lead to different nuclear configurations for excited and ground states, the disparity between configurations must be smaller than those in the other polymolybdates. It is possible that more nested ground and excited-state potential surfaces in $[\text{Mo}_6\text{O}_{19}]^{2-}$ increase the rate of the l.m.c.t. relaxation and consequently decrease the value of $\varphi_{\text{e.t.}}$. In $[\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{n-}$ ($\text{M} = \text{Cr}^{\text{III}}$,

$\text{Rh}^{\text{III}}, \text{Fe}^{\text{III}}$ with $n = 3$; Ni^{II} with $n = 4$) the ($\text{O}^{2-} \longrightarrow \text{Mo}^{\text{VI}}$) l.m.c.t. is similar in delocalization and energy to the lowest-energy c.t. state of $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ but there are also ($\text{O}^{2-} \longrightarrow \text{M}$) l.m.c.t. and metal-centred, d-d, excited states lying at lower energies. Although the conversion of ($\text{O}^{2-} \longrightarrow \text{Mo}^{\text{VI}}$) l.m.c.t. into lower-lying d-d states seems to be insignificant, it is still possible that conversions to lower-lying ($\text{O}^{2-} \longrightarrow \text{M}$) l.m.c.t. states are responsible for the small yields measured with $[\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{n-}$ ($\text{M} = \text{Cr}^{\text{III}}, \text{Rh}^{\text{III}}, \text{Fe}^{\text{III}}$ with $n = 3$; Ni^{II} with $n = 4$).

Acknowledgements

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* Series based on the respective photoreactivities of the hexa- and octamolybdates and quantum yields reported in ref. 5.