

Photochemistry, Spectroscopy, and X-Ray Structure of an Intermolecular Charge-transfer Complex between an Organic Substrate and a Polyoxometallate, $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}\cdot 6$ (tetramethylurea)

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A photosensitive complex between an organic substrate, 1,1,3,3-tetramethylurea (TMU), and the heteropoly acid, $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}$ of stoichiometry $[(\text{TMU})_2\text{H}]_3\text{PMo}_{12}\text{O}_{40}$, (**1**), has been characterized in solution and in the solid state; irradiation into the low energy absorption bands of (**1**) in solution or in the solid state results in the immediate photoreduction of the polyoxometallate by the TMU.

The complex charge-transfer electron absorption manifold of some soluble metal oxide species including heteropoly acids of Mo and W is known to shift substantially to lower energy on going from water to organic solvents.^{1,2} These medium-induced bathochromic spectral shifts render some polyoxometallate species highly photosensitive. In addition, they are directly related to the use of polyoxometallates as catalysts for the photochemical dehydrogenation of organic substrates.³ After substantial effort, an organic substrate and solvent, 1,1,3,3-tetramethylurea (TMU), has been found that produces red shifts in the electronic absorption spectra of polyoxometallates as large as any cited in the literature. Furthermore this organic substrate interacts with one poly-

oxometallate, $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}$ to produce an isolable intermolecular complex of high experimental tractability.

Although the wavelength maximum for the heteropoly compound, $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}$, is little perturbed on going from water ($\lambda_{\text{max.}} = 310$ nm) to TMU ($\lambda_{\text{max.}} = 308$ nm), the low energy absorption tail is quite shifted to the visible in TMU, Figure 1(b). Irradiation into this low energy absorption tail results in oxidation of TMU and production of the well-characterized⁴ class II mixed-valence heteropoly blue chromophore of $\alpha\text{-PMo}_{12}\text{O}_{40}^{4-}$ by pseudo-first-order kinetics, Figure 1(a). The production of this reduced complex is proportional to the light absorbed by the system in this spectral region, Figures 1(a) and (b).

A crystalline solid complex between $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}$ and TMU with the same spectral and photochemical properties as the TMU solution of $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}$ above can be isolated. If an aqueous solution of 1 equiv. of the pale yellow complex, $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$, is treated with 6 equiv. of colourless TMU, a dark orange precipitate of crude (**1**) forms. Several recrystallizations from acetonitrile in the dark produce a 70% yield of dark orange prisms that analyse for $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}\cdot 6(\text{TMU})$.† An ORTEP plot with the urea oxygen atoms, the polyoxo oxygen atom, O(5a), and the phosphorus atom labelled is shown in Figure 2 (atoms with a '+' are generated by symmetry operations). The six TMU molecules are hydrogen-bonded to each other in 3 pairs, 2 of which are indicated [hollow lines between O(b)-O(b)+ and O(c)-O(c)+]; thus the most accurate formulation for (**1**) is $[(\text{TMU})_2\text{H}]_3\alpha\text{-PMo}_{12}\text{O}_{40}$. The structure of the $\alpha\text{-PMo}_{12}\text{O}_{40}^{3-}$ moiety is unperturbed relative to the parent heteropoly compound,⁵ and the TMU-polyoxo oxygen interactions are not covalent. Indeed, the shortest nonbonded distance [O(5a)-O(a)+] is 2.894 Å.

The electronic interactions between the polyoxo moiety and the TMU moieties responsible for the shifts in the absorption spectrum and photoredox spectrum, Figure 1(b), are disrupted when (**1**) is dissolved in acetonitrile. The ¹⁷O (22% ¹⁷O-enriched)‡ n.m.r. spectra of (**1**) in acetonitrile and TMU confirm that the $\alpha\text{-PMo}_{12}\text{O}_{40}^{3-}$ moiety is structurally unper-

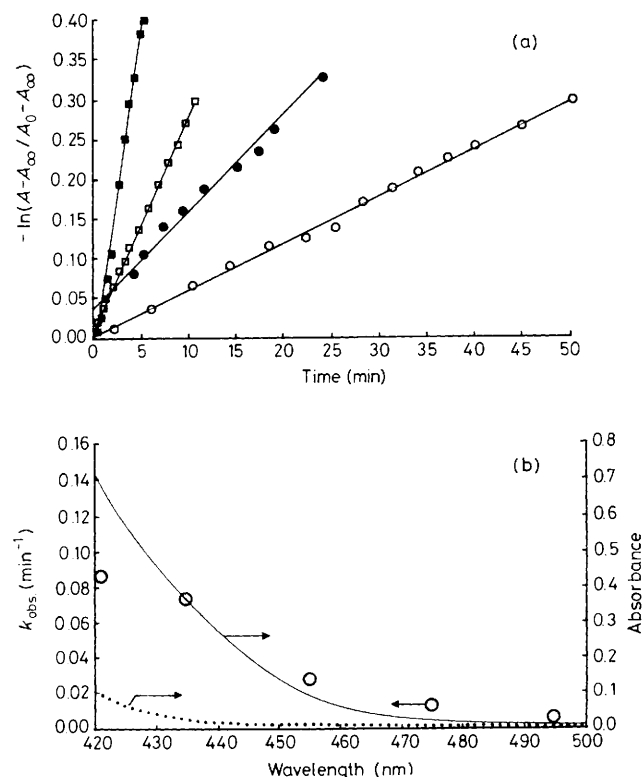


Figure 1. (a) Representative kinetics plots for irradiation of 0.50 mM (**1**) in TMU at 25°C with 1000 W Xe lamp using cut-off filters >420 nm (■), >455 nm (□), >475 nm (●), or 495 nm (○); A_{∞} measured at λ_{max} for $\text{PMo}_{12}\text{O}_{40}^{4-}$ (723 nm); A_{∞} determined empirically. (b) Spectra of $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}$ in TMU (—), (**1**), and in H_2O (·····), both 0.24 mM in 10 mm cell at 25°C (right y axis) and pseudo-first-order rate constants (circles) for production of $\text{PMo}_{12}\text{O}_{40}^{4-}$ plotted as function of cut-off of incident light (left y axis).

† Satisfactory analytical data for C, H, Mo, N, P were obtained.

Crystal data: $\text{C}_{30}\text{H}_{75}\text{Mo}_{12}\text{N}_{12}\text{O}_{46}\text{P}$, $M = 2522.27$, monoclinic, $C2/c$, $a = 21.28(1)$, $b = 13.83(1)$, $c = 24.69(2)$ Å, $\beta = 100.95(4)^\circ$, $U = 7136(6)$ Å³, $D_c = 2.35$, $D_M = 2.37(2)$ g cm⁻³, $Z = 4$. 4 152 Reflections with $F_o > 3\sigma(F_o)$ were measured using Mo- K_α radiation. The structure was solved by Patterson techniques and direct methods and refined to a final $R = 0.0508$.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

‡ ¹⁷O n.m.r. (in p.p.m. relative to H_2^{17}O). In CD_3CN : 1103.73 (terminal O), 671.39 and 646.72 (doubly bridging O); in TMU: 942.67 (terminal O), 589.83, and 548.91 (doubly bridging O); triply bridging O atom not enriched in ¹⁷O.

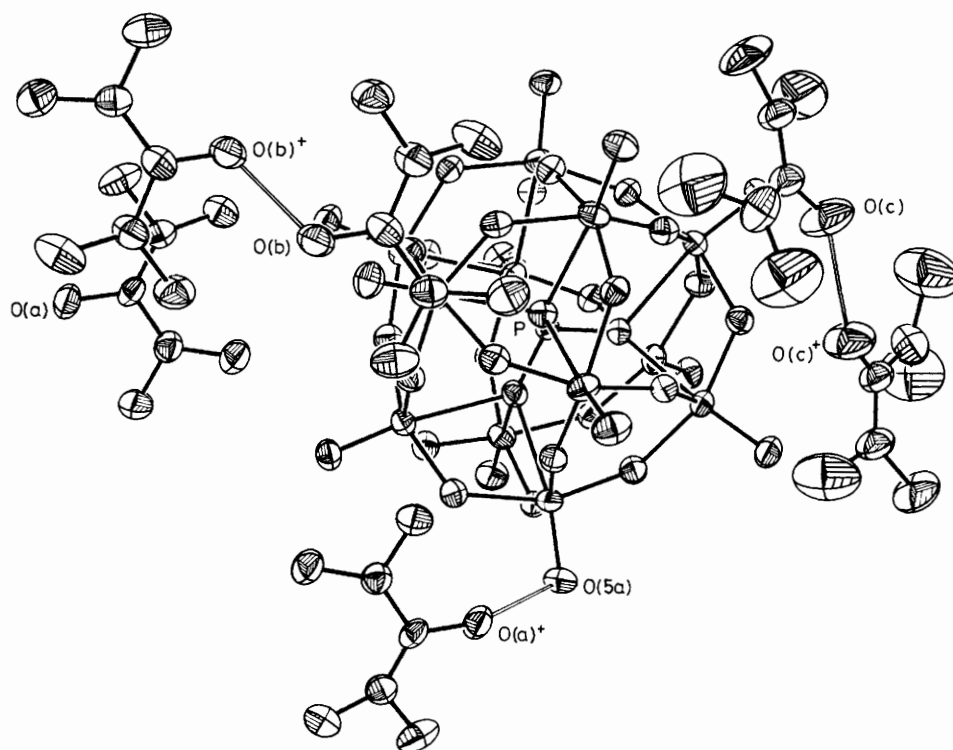


Figure 2. ORTEP plot of (1). The thermal ellipsoids are drawn at the 30% probability level.

turbed in solution as in the solid state and that dissolution in acetonitrile results in disruption of the TMU–polyoxo electronic interactions. The spectroscopic and photochemical properties of (1) define it to be a new form of Mulliken electron donor–acceptor complex, between an organic donor and an inorganic heteropoly acid acceptor.

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References

- 1 M. T. Pope, 'Heteropoly and Isopoly Oxometalates,' Springer-Verlag, Berlin, 1983.
- 2 F. Umland and G. Wuensch, *Z. Anal. Chem.*, 1967, **225**, 362.
- 3 C. L. Hill and D. A. Bouchard, *J. Am. Chem. Soc.*, 1985, **107**, 5148.
- 4 C. Sanchez, J. Livage, J. P. Launay, M. Fournier, and Y. Jeannin, *J. Am. Chem. Soc.*, 1982, **104**, 3194.
- 5 C. J. Clark and D. Hall, *Acta Crystallogr., Sect. B*, 1976, **32**, 1545.