# Photochemical Studies of the Alkylammonium Molybdates. Part 4.[1] Electron Spin Resonance Study of an Irradiated Single Crystal of Hexakis(isopropylammonium) Dihydrogen Octamolybdate Dihydrate

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A single-crystal e.s.r. study of the formation of $Mo^{5+}$ on irradiation of the title compound $[NH_3Pr^i]_6[H_2Mo_8O_{28}]\cdot 2H_2O$ has been carried out at room temperature using 100-kHz modulation. The main line arising from the naturally abundant $^{96}Mo(I = 0)$ is split into three hyperfine lines (1 : 2 : 1) owing to superhyperfine interaction with two equivalent hydrogen atoms. The hyperfine lines due to $^{95}Mo$ and $^{97}Mo$ could not be analysed because of lack of resolution of weaker resonances. The principal components of the $g$ and $^1H$ superhyperfine tensors are $g_1$ 1.955, $g_2$ 1.941, $g_3$ 1.897, $|A_1|$ $10.14 \times 10^{-4}$ $cm^{-1}$, $|A_2|$ $9.28 \times 10^{-4}$ $cm^{-1}$, and $|A_3|$ $8.69 \times 10^{-4}$ $cm^{-1}$. From the correlation with $X$-ray crystal-structure data, it is proposed that the formation of $Mo^VO_4(OH)_2$ in a $MoO_6$ octahedral site is a highly probable mechanism for the u.v.-induced colouration.

HEXAKIS(ISOPROPYLAMMONIUM) DIHYDROGEN OCTAMOLYBDATE DIHYDRATE, $[NH_3Pr^i]_6[H_2Mo_8O_{28}]\cdot 2H_2O$, was found during a preparation of photochromic alkylammonium molybdates.[1] The crystal structure of this compound has been determined using $X$-ray diffraction ($R$ 0.036). The compound is triclinic with space group $P\bar{1}$, and the unit cell contains one formula unit ($Z = 1$) with dimensions $a = 10.66$, $b = 12.29$, $c = 9.65$ Å, $\alpha = 104.6$, $\beta = 82.1$, and $\gamma = 96.5°$.[2] The octamolybdate unit is built up from distorted $MoO_6$ octahedra sharing edges and corners. Figure 1 shows a view of the unit cell along the $c$ axis. The hydrogen-atom positions in the $[H_2Mo_8O_{28}]^{6-}$ anion could not be deduced exactly, but it is clear that they are attached to the O(6) and O(6′) atoms which form the terminal Mo–O bond.[2,*] The nearest-neighbour molecules in the crystal are linked by hydrogen bonds to water molecules and $[NH_3Pr^i]^+$ ions. When the transparent colourless crystal (or white powder) is irradiated with u.v. light ($\lambda \geqslant 313$ nm), a violet colouration is observed and the existence of a $Mo^{5+}$ centre has been established by an e.s.r. study of the polycrystalline sample.[1] The main objective of the present work was to study this photochemical process with the help of e.s.r. spectroscopy of the irradiated single crystal.

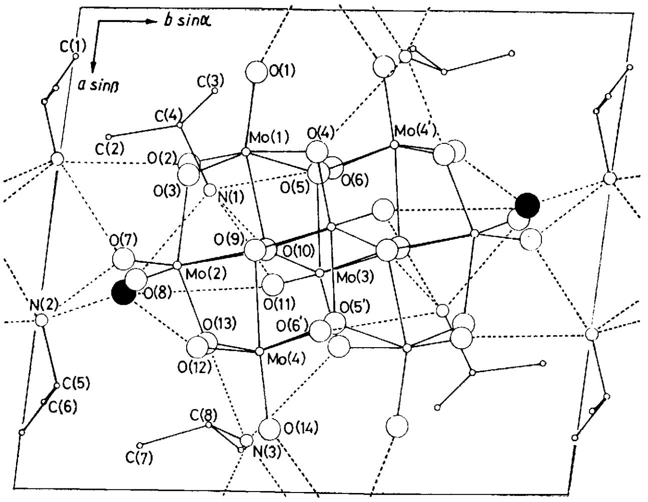

FIGURE 1 Projection of the unit cell of $[NH_3Pr^i]_6[H_2Mo_8O_{28}]\cdot 2H_2O$ along the $c$ axis on the normal plane. Filled circles represent water molecules. The atom-numbering system used for the Mo, O, C, and N atoms is shown

EXPERIMENTAL

E.s.r. spectra were recorded at room temperature with a Varian E12 $X$-band spectrometer using 100-kHz field modulation. Single crystals of the compound were grown from an aqueous solution (10 $cm^3$) containing bis(isopropylammonium) dimolybdate dihydrate (5 g) at room temperature in the dark for 2 weeks.[1] An idealized representation of such a crystal is given in Figure 2 together with the body-fixed orthogonal axis system ($X$, $Y$, $Z$) to which the results are referred. The $X$ direction is precisely located relative to one of the edges shown and is identical to the crystallographic $c$ axis; the $Y$ direction is perpendicular to the flat face, and the crystallographic $a$ axis is perpendicular to the $Y$ axis. Ultraviolet irradiation ($\lambda \geqslant 313$ nm) for periods of *ca.* 30 min was carried out using a 500-W super-high-pressure mercury lamp in conjunction with filters. After the irradiation the crystal was mounted on a quartz

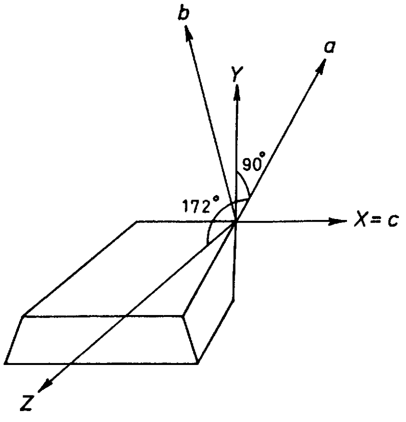

FIGURE 2 Sketch of the single crystal, indicating rectangular $X$,$Y$,$Z$, and crystallographic $a$,$b$,$c$, axes

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* Similar anionic structure has been found in $[NH_4]_6[Mo_8O_{27}]\cdot 4H_2O$ [3] whose structure consists of infinite chains of octamolybdate units linked through a common oxygen atom corresponding to O(6) or O(6′) in Figure 1.

[1] Part 3, T. Yamase and T. Ikawa, *Bull. Chem. Soc. Japan*, 1977, **50**, 746.

[2] M. Isobe, T. Yamase, T. Ikawa, and F. Marumo, *Acta Cryst.*, submitted for publication.

[3] I. Böschen, B. Buss, and B. Krebs, *Acta Cryst.*, 1974, **B30**, 48.

rod (diameter 3 mm) with silicon grease. At room temperature (under aerobic conditions), the decay of the e.s.r. signals due to the back reaction was small during measurements. E.s.r. data were taken at least every 10° in each of three orthogonal $XY$, $YZ$, and $ZX$ planes. After completion of the e.s.r. study, the orientation of the crystallographic axes ($a$, $b$, $c$) with respect to the body-fixed orthogonal axes ($X$, $Y$, $Z$) was determined by oscillation photographs.

## RESULTS

Figure 3 shows the observed e.s.r. spectrum of a representative sample. It contains 1 : 2 : 1 triplets at *g ca.* 1.9, covering a region of *ca.* 20 G.* The 1 : 2 : 1 intensity ratio was retained at all orientations and the triplet splittings showed little anisotropy. The $g$ values of these resonances show slight anisotropy, varying between 1.90 and 1.96. This indicates the existence of two magnetically equivalent hydroxide groups interacting with a $Mo^{5+}$ ion (see below). Hyperfine lines from $^{95}Mo$ (15.7%) and $^{97}Mo$ (9.5%) could be resolved at only a few orientations, and consisted of six very weak lines (splitting constant, $50 \times 10^{-4}$—$60 \times 10^{-4}$ cm$^{-1}$) upon each of which were superimposed triplet superhyperfine lines. However, these lines are too weak to be observed and analysed at all orientations.†

The spectra were interpreted in terms of the spin Hamiltonian (1) with spin $S = \frac{1}{2}$ and $I_H = \frac{1}{2}$. In Figure 4

$$\mathscr{H} = \beta H \cdot g \cdot S + \sum_{H} I_H \cdot A_H \cdot S \qquad (1)$$

values of $g^2$ and $g^2K^2$ are plotted against an arbitrary angle of rotation of the magnetic field in the $XY$, $YZ$, and $ZX$ planes; $K$ is the superhyperfine splitting. The $g^2$ and $g^2K^2$ values in the three planes were least-squares fitted to equations of the form (2) and (3). The fitting constants

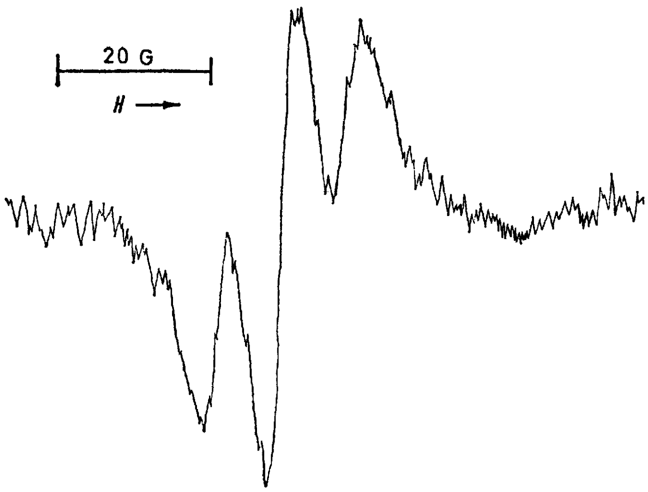

FIGURE 3 E.s.r. spectrum of an irradiated single crystal ($H_0$ is perpendicular to the $Y$ axis)

$$g^2(\phi) = B_1 \cos^2\phi + 2B_2 \cos\phi \sin\phi + B_3 \sin^2\phi \qquad (2)$$

$$g^2K^2(\phi) = C_1 \cos^2\phi + 2C_2 \cos\phi \sin\phi + C_3 \sin^2\phi \qquad (3)$$

can be identified with the components of the $g^2$ and $g^2K^2$ tensors: $B_1 = (g^2)_{ii}$, $B_2 = (g^2)_{ij}$, $B_3 = (g^2)_{jj}$, $C_1 = (g^2K^2)_{ii}$, $C_2 = (g^2K^2)_{ij}$, and $C_3 = (g^2K^2)_{jj}$, where $i,j = X,Y$, $Y,Z$, and $Z,X$. The tensors were then diagonalized to give the principal values and direction cosines of $g$ and $A$. The Hamiltonian parameters so obtained are listed in the Table.

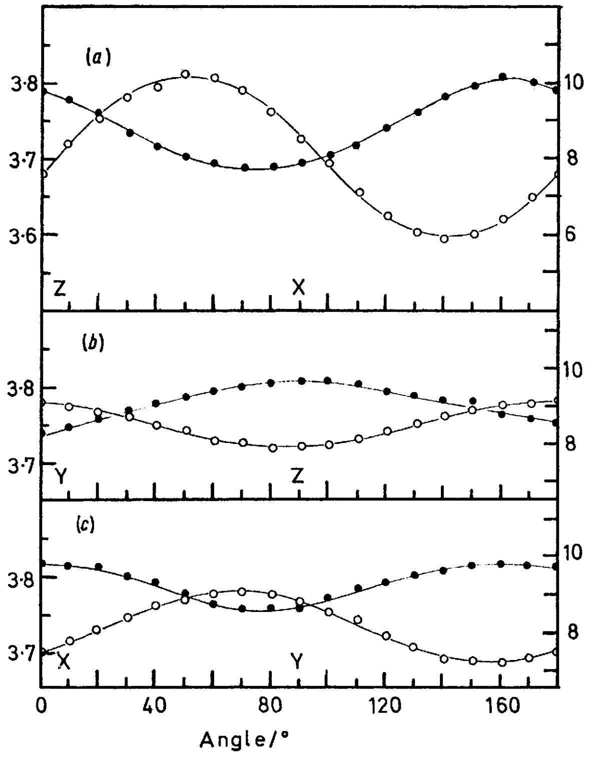

FIGURE 4 Angular dependence of $g^2$ (○) and $g^2K^2$(●) in the $ZX$ (*a*), $YZ$, (*b*), and $XY$ (*c*) planes

$g$ and $^1H$ superhyperfine tensors

| | Direction cosines with respect to | | |
|---|---|---|---|
| Principal value | *x* | *y* | *z* |
| $g_1$ 1.955 | 0.680 | 0.399 | 0.615 |
| $g_2$ 1.941 | 0.200 | −0.899 | 0.390 |
| $g_3$ 1.897 | 0.689 | −0.154 | −0.709 |
| $\lvert A_1 \rvert$ $10.14 \times 10^{-4}$ cm$^{-1}$ | 0.378 | −0.045 | −0.925 |
| $\lvert A_2 \rvert$ $9.28 \times 10^{-4}$ cm$^{-1}$ | −0.135 | 0.986 | −0.103 |
| $\lvert A_3 \rvert$ $8.69 \times 10^{-4}$ cm$^{-1}$ | 0.914 | 0.160 | 0.373 |

We estimate the averages $g_0 = (g_1 + g_2 + g_3)/3$ and $A_0 = (A_1 + A_2 + A_3)/3$ to be 1.931 and $9.37 \times 10^{-4}$ cm$^{-1}$ respectively.

Several papers have reported ligand superhyperfine interactions with $Mo^{5+}$,[4-7] but we can find none which assigns the hydrogen interaction with $Mo^{5+}$ to bonding between the metal ion and hydroxide ligand.

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* Throughout this paper: 1 G = $10^{-4}$ T.

† An irradiated single crystal of $[NH_3Pr^i]_2[Mo_2O_7]\cdot 2H_2O$ gave six observable weak satellite lines due to $^{95}Mo$ and $^{97}Mo$ at all orientations. Unfortunately the crystal-structure determination has not been made yet.

[4] P. T. Manoharan and M. T. Rogers, *J. Chem. Phys.*, 1965, **49**, 5510.

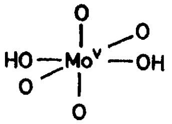
[5] N. Pariyadath, W. E. Newton, and E. I. Stiefel, *J. Amer. Chem. Soc.*, 1976, **98**, 5388.

[6] T. Imamura, G. P. Haight, and R. L. Belford, *Inorg. Chem.* 1976, **15**, 1047.

[7] W. Levason, C. A. McAuliffe, and B. J. Sayle, *J.C.S. Dalton*, 1976, 1177.

## DISCUSSION

The line separation (9.8—11 G) of the 1 : 2 : 1 triplet was observed at all rotations of the magnetic field in the $XY$, $YZ$, and $ZX$ planes. It indicates the existence of two magnetically equivalent hydrogens interacting with $Mo^{5+}$. Two hydroxide groups of O(6)–H and O(6′)–H are crystallographically equivalent and are related by a centre of inversion in the unit cell. The possibility of a triplet arising from spin coupling of $Mo^{5+}$ and two H atoms of O(6)–H and O(6′)–H seems unlikely, for in this case the $g$ values would have to be nearly isotropic and approximately equal to the free-electron value (2.002 3) due to electron delocalization on to the two distant H atoms. In view of the observed $g$ values, the most likely paramagnetic species is (1).



(1)

It is reasonable to assume that the formation of species (1) results from internal hydrogen abstraction by oxygen at the Mo(4) or Mo(4′) site where a hydroxide group is originally co-ordinated. Figure 5 shows the bond distances and bond angles in the environment of the Mo(4) site, taken from $X$-ray diffraction data. The short distance (2.93 Å) between $O(H_2O)$ and O(12) indicates a strong hydrogen bond H–O–H $\cdots$ O(12), and this is confirmed by the fact [2] that the H atom of the water molecule and O(12) approach (2.16 Å) each other more closely than the sum of the van der Waals radii of H (1.20 Å) and O (1.39 Å).[8] The hydrogen atom in this scheme may be photochemically transferred to O(12), resulting in the superhyperfine line due to two H atoms. Two H atoms would then be bound to the two inequivalent (*cis*) oxygens, O(12) and O(6′), and should exhibit two distinguishable sets of 1 : 1 doublet superhyperfine lines, although the principal values of the two tensors should be nearly equal. However, this hypothesis seems unlikely since the superhyperfine structure found is a 1 : 2 : 1 triplet at all rotations of the magnetic field. Furthermore, the fact [2] that the H atom of the water molecule is located at the longer distance (4.96 Å) to O(13) excludes the possibility of hydrogen transfer from a co-ordinated water molecule to O(13).

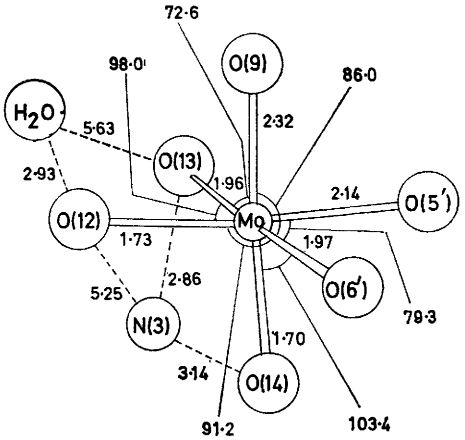


FIGURE 5 Bond distances (Å) and angles (°) in the environment of the Mo(4) site. Positions of H atoms are omitted for clarity, and there is some uncertainty in the H–O and H–N distances.[2] The $H_2O$-filled circle represents an O atom of the water molecule

Hydrogen transfer from N(3) to O(13) upon u.v. irradiation seems highly probable, assuming the magnetic equivalence of two H atoms co-ordinated to two nearly equivalent (*trans*) oxygens associated with a O(13)–Mo(4)–O(6′) angle of 156.8° and with nearly equivalent Mo(4)–O(13) and Mo(4)–O(6′) bond distances. The distance (2.04 Å) [2] between the H and O(13) atoms involved in the proposed hydrogen abstraction from N(3) is close to the sum of the van der Waals radii ($r_H$ 0.82 Å, $r_O$ 1.14 Å) of the atoms involved.[8] This renders the postulated hydrogen transfer eminently reasonable, even if the positional parameters of H atoms are not always precise.[2]

Concerning the formation of $Mo^{5+}$ at the Mo(4) site, one explanation is that u.v.-induced charge transfer takes place in the Mo–O bond, perhaps in the Mo(4)–O(14) bond where the terminal bond length is close to that for a double bond. However, from the results described here, it is difficult to explain how the hydrogen transfer from N(3) to O(13) is accompanied by charge transfer in the Mo(4)–O(14) bond. As is obvious from the $g$ tensor, the crystal field at the $Mo^{5+}$ site is of less than axial symmetry. The crystal field is of such low symmetry that an analysis of the observed $g$ and superhyperfine tensors would be very difficult.[9] The large isotropic H(O) value of $9.37 \times 10^{-4}$ cm$^{-1}$ suggests that the isotropic coupling constant is not related to the spin density on the O atom * but to the direct spin polarization between $Mo^{5+}$ and H atoms producing positive spin density at the proton.

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* In this case the observed isotropic value requires at least 37% spin density on the O atom using the isotropic proton hyperfine splitting of −27 G in the hydroxyl radical.[10] This value is too large to be in agreement with the quite substantial spin distribution on the $Mo^{5+}$ centre. The spin density on the O atom would be further increased due to ionic bonding in O–H.[11]

[8] J. T. Edward, *J. Chem. Educ.*, 1970, **47**, 261.

[9] W. Low and E. L. Offenbacher, *Solid State Phys.*, 1965, **17**, 135.

[10] P. W. Atkins and M. C. R. Symons, ' The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967, p. 104.

[11] W. Derbyshire, *Mol. Phys.*, 1962, **5**, 225.