Photochemical Studies of the Alkylammonium Molybdates. Part 6.[1] Photoreducible Octahedron Site of $[Mo_7O_{24}]^{6-}$ as determined by Electron Spin Resonance

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The Mo^V centre formed by u.v.-irradiation of a single crystal of $[NH_3Pr]_6[Mo_7O_{24}]\cdot 3H_2O$ has been studied by e.s.r. at room temperature. The e.s.r. spectra are attributed to a localized octahedral $Mo^VO_5(OH)$ site, resulting from transfer of a hydrogen bonding proton from a $[NH_3Pr]^+$ nitrogen to a bridging oxygen atom. The principal values of the g, A_{Mo}, and A_H tensors are $g_1 = 1.895$, $g_2 = 1.925$, $g_3 = 1.937$, $A_{Mo(1)} = 2.34 \times 10^{-3}$, $A_{Mo(2)} = 4.20 \times 10^{-3}$, $A_{Mo(3)} = 6.99 \times 10^{-3}$, $A_{H(1)} = 8.15 \times 10^{-4}$, $A_{H(2)} = 9.14 \times 10^{-4}$, and $A_{H(3)} = 12.5 \times 10^{-4}$ cm^{-1}. Analysis of the e.s.r. parameters indicates the direct spin polarization between the paramagnetic electron orbital of molybdenum and the hydrogen orbital. From the direction of the largest principal value for the A_H tensor, which is approximately parallel to the $H(O) \cdots Mo^V$ direction, the paramagnetic site in seven MoO_6 octahedra is determined in correlation with the *X*-ray crystal structure data. It is proposed that Mo^V formation occurs at an end of three octahedra in a line in the central horizontal level of the $[Mo_7O_{24}]^{6-}$ configuration, where the molybdenum atom has a long Mo–O bond (2.5 Å).

Photoredox reaction of alkylammonium polymolybdate in aqueous solutions, leading to the formation of Mo^V in polymolybdate and $^{\bullet}OH$ as an oxidation product of H_2O, is interesting from the standpoint of the water-photoelectrolysis achieved by the photogalvanic cell.[1,2] Based on the fact that an initial step for the solution photochemistry corresponds to the photochemical step for the alkylammonium polymolybdate solid, e.s.r. studies of the irradiated single crystals have been carried out to achieve a better understanding of the solution photochemistry.[1] The localized Mo^V site for the u.v.-irradiated hexakis(isopropylammonium) dihydrogenoctamolybdate(VI) dihydrate $[NH_3Pr^i]_6[H_2Mo_8O_{28}]\cdot 2H_2O$ has been identified as $Mo^VO_4(OH)_2$ and observed at the octahedral site where the molybdenum atom originally co-ordinates a hydroxide group.[3] The u.v.-induced transfer of a proton occurs from a $[NH_3Pr^i]^+$ nitrogen to the bridging oxygen atom which is *trans* with respect to the originally co-ordinated hydroxide group. U.v.-irradiation of a single crystal of hexakis(isopropylammonium) heptamolybdate(VI) trihydrate $[NH_3Pr^i]_6[Mo_7O_{24}]\cdot 3H_2O$ results in the formation of a localized $Mo^VO_5(OH)$ site.[1] The assignment of the photoreducible molybdenum atom in seven MoO_6 octahedra has been impossible, since the final *R* value of 0.060 for crystal structure data makes interatomic distances and angles of the hydrogen bonds remain uncertain.[4] It has been realized that the three-dimensional studies of hexakis(propylammonium) heptamolybdate(VI) trihydrate $[NH_3Pr]_6[Mo_7O_{24}]\cdot 3H_2O$ as a heptamolybdate allows determination ($R = 0.035$) of the cation configurations within the structure.[4] The geometry of $[Mo_7O_{24}]^{6-}$ for $[NH_3Pr]_6[Mo_7O_{24}]\cdot 3H_2O$ consists of seven MoO_6 octahedra condensed by edge sharing into a structure that has the approximate point symmetry $2mm(C_{2v})$. The geometry is similar to that for $[NH_4]_6[Mo_7O_{24}]\cdot 4H_2O$ or $[NH_3Pr^i]_6[Mo_7O_{24}]\cdot 3H_2O$.[4,5] Figure 1 shows the arrangement of $[Mo_7O_{24}]^{6-}$ in terms of polyhedra, in which three octahedra are approximately in a line in the central horizontal level, two are attached forward at a level above, and two more forward at a level below. In the idealized heptamolybdate ion, there are three distinct molybdenum atoms, all in distorted octahedral co-ordination: Mo(1), Mo(2), Mo(3), and Mo(4); Mo(7); and Mo(5) and Mo(6). The octahedral site of Mo(5) or Mo(6) differs from other molybdenum sites by having a long Mo–O bond (2.5 Å).[4]

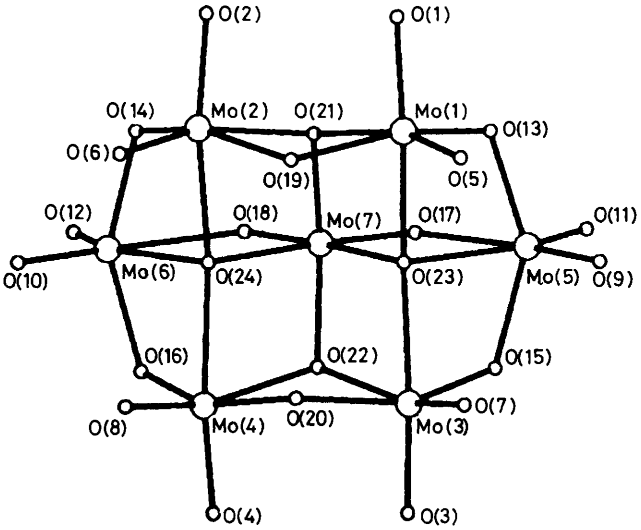

Figure 1. Structure and atomic numbering scheme for $[Mo_7O_{24}]^{6-}$

We decided to study the paramagnetic site in the u.v.-irradiated single crystal of $[NH_3Pr]_6[Mo_7O_{24}]\cdot 3H_2O$, since e.s.r. spectra result from a localized paramagnetic site in the molecule, in order to determine which site in seven condensed octahedra is paramagnetic.

Experimental

Solid $[NH_3Pr]_6[Mo_7O_{24}]\cdot 3H_2O$ was synthesised using an already published method.[6] Single crystals were obtained by slow evaporation from an aqueous solution. The crystallogaphic structure has been reported by us.[4] The crystal belongs to the space group $P\bar{1}$, the two molecules being related by a centre of inversion: $a = 14.118$, $b = 15.977$, $c = 11.368$ Å, $\alpha = 90.23$, $\beta = 93.00$, $\gamma = 111.79°$, and $Z = 2$. An orthogonal axis system was chosen in the crystal: the y axis coincident with the c direction, the z axis perpendicular to the flat face

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Non-S.I. unit employed: 1 G = 10^{-4} T.

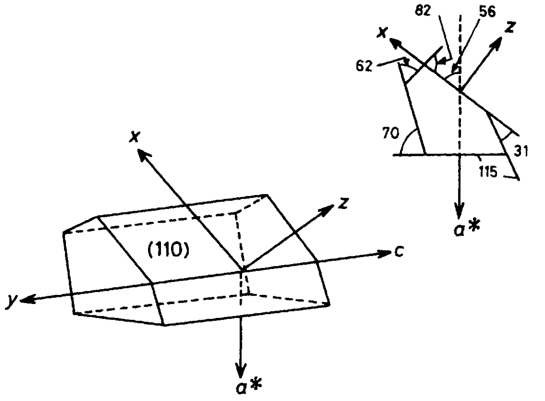

Figure 2. E.s.r. reference axes (*xyz*) and crystallographic directions for an idealized crystal of $[NH_3Pr]_6[Mo_7O_{24}]\cdot 3H_2O$

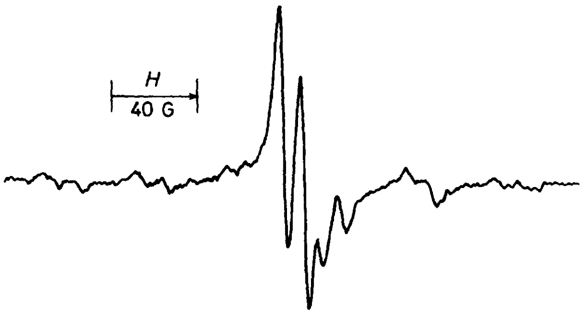

Figure 3. E.s.r. spectrum of a u.v.-irradiated single crystal of $[NH_3Pr]_6[Mo_7O_{24}]\cdot 3H_2O$, with H_0 paralleling the *c* axis in the *yz* plane

Table. Electron spin resonance parameters for Mo^V centre

Principal values Mo^V centre			Angles (°) with respect to		
			x	y	z
g [a]	g_1	1.895	32.0	72.3	64.2
	g_2	1.925	111.1	105.8	26.9
	g_3	1.937	112.9	24.0	83.0
	g_0	1.919			
A_{Mo} [b]	$A_{Mo(1)}$	2.34	109.0	130.6	46.7
	$A_{Mo(2)}$	4.20	101.6	40.9	51.5
	$A_{Mo(3)}$	6.99	22.5	93.8	67.9
	$A_{Mo(0)}$	4.51			
A_H [c]	$A_{H(1)}$	8.15	33.4	63.7	71.0
	$A_{H(2)}$	9.14	114.2	26.3	99.7
	$A_{H(3)}$	12.5	111.5	89.5	21.5
	$A_{H(0)}$	9.93			

[a] $g_0 = (g_1 + g_2 + g_3)/3$. [b] A_{Mo}: units in 10^{-3} cm^{-1}, $A_{Mo(0)} = [A_{Mo(1)} + A_{Mo(2)} + A_{Mo(3)}]/3$. [c] A_H: units in 10^{-4} cm^{-1}, $A_{H(0)} = [A_{H(1)} + A_{H(2)} + A_{H(3)}]/3$.

of (1 1 0), and the x axis perpendicular to y and z. This orthogonal axis system and the crystal morphology are indicated in Figure 2. The orientation of the body-fixed orthogonal axes with respect to the crystallographic axes was determined by both oscillation and Weissenberg photographs. The single crystal was irradiated at room temperature with u.v.-light of $\lambda \geqslant 313$ nm. After irradiation, the sample is reddish brown. A spectrometer Varian E-12 *X*-band (100 kHz field modulation) was used for the e.s.r. study and the experiments were performed at room temperature according to the method described in previous papers.[1,3] The decay of the e.s.r. signals due to the back reaction was small during measurements;[6] and data were taken at least every 10° in each of three orthogonal planes.

Results

An example of the e.s.r. spectrum obtained with a u.v.-irradiated single crystal of $[NH_3Pr]_6[Mo_7O_{24}]\cdot 3H_2O$ is given in Figure 3. The two intense central lines (1 : 1) with a linewidth equal to *ca.* 5 G clearly result from the superhyperfine coupling with ^1H ($I = \frac{1}{2}$). On each side of the central spectrum, six lines of low intensity are detected. The splittings between two consecutive lines of the central spectrum are the same as those between two consecutive side bands, and the intensity between a central and a side signal is *ca.* 5%. These observations indicate that the side-lines result from the hyperfine coupling with the two molybdenum isotopes $^{95,97}Mo$ in natural abundance (25.15%) which have the same nuclear spin ($I = \frac{5}{2}$) and nearly the same magnetic moment so that it is not possible to resolve the separate hyperfine lines and that each of the hyperfine lines is resolved into two superhyperfine lines due to ^1H. The occurrence of the $^{95,97}Mo$ hyperfine and ^1H superhyperfine structures is characteristic of an unpaired electron localized on one molybdenum only. Furthermore the lines are narrow and no exchange broadening is observed. All these observations are in accordance with the paramagnetic site $Mo^VO_5(OH)$ localized in seven condensed octahedra. The spectra were interpreted in terms of the spin Hamiltonian [equation (1)] with $S = \frac{1}{2}$, $I_{Mo} = \frac{5}{2}$, and $I_H = \frac{1}{2}$. The final e.s.r. parameters were obtained by an iterative least-squares

$$\mathscr{H} = \beta HgS + I_{Mo}A_{Mo}S + I_HA_HS \qquad (1)$$

procedure utilizing exact diagonalizations of the Hamiltonian matrix, according to the previous method.[3] The results are given in the Table. In Figure 4 the angular variations of experimental g, A_{Mo}, and A_H values, in the planes xy, yz, and zx, are reported.

U.v.-irradiation of the deaerated aqueous solution (13.6 mmol dm^{-3}) of $[NH_3Pr]_6[Mo_7O_{24}]\cdot 3H_2O$ revealed the presence of two paramagnetic species of $\langle g \rangle = 1.921$ and 1.910 as shown in Figure 5 where a well defined signal at $\langle g \rangle = 1.921$ developed with weak satellite lines ($\langle A \rangle \approx 50$ G $= 4.5 \times 10^{-3}$ cm^{-1}) due to $^{95,97}Mo$. Observable $\langle g \rangle$ and $\langle A \rangle$ values are almost the same as for the photolyte of a solution of $[NH_3Pr^i]_6[Mo_7O_{24}]\cdot 3H_2O$,[1] suggesting that the formation of the two paramagnetic species found for the photolyte is hardly affected by the variation of the alkylammonium cations.[6]

Discussion

The Table shows the principal values of the g, hyperfine (A_{Mo}), and superhyperfine (A_H) tensors. It has been reported that the oxygen-containing ligands for molybdenyl compounds are characterized by $g_\perp > g_\parallel$ and that this can be qualitatively explained in terms of a small spin-orbit coupling constant (152 cm^{-1}) of oxygen atoms bonded to Mo.[7] The relative magnitude of the components of the g tensor (Table) supports this conclusion, if $g_\perp = (g_2 + g_3)/2$ and $g_\parallel = g_1$ are taken. The usual difficulty in analysis of e.s.r. parameters is determining the signs of the components of the hyperfine and superhyperfine tensors. It is most likely that all of the principal values of the $^{95,97}Mo$ splitting tensors have the same sign, since the thus derived isotropic component (4.51×10^{-3} cm^{-1}) is quite similar to that (4.5×10^{-3} cm^{-1}) observed for the paramagnetic species of $\langle g \rangle = 1.921$ in the photolyte (Figure 5) which gave

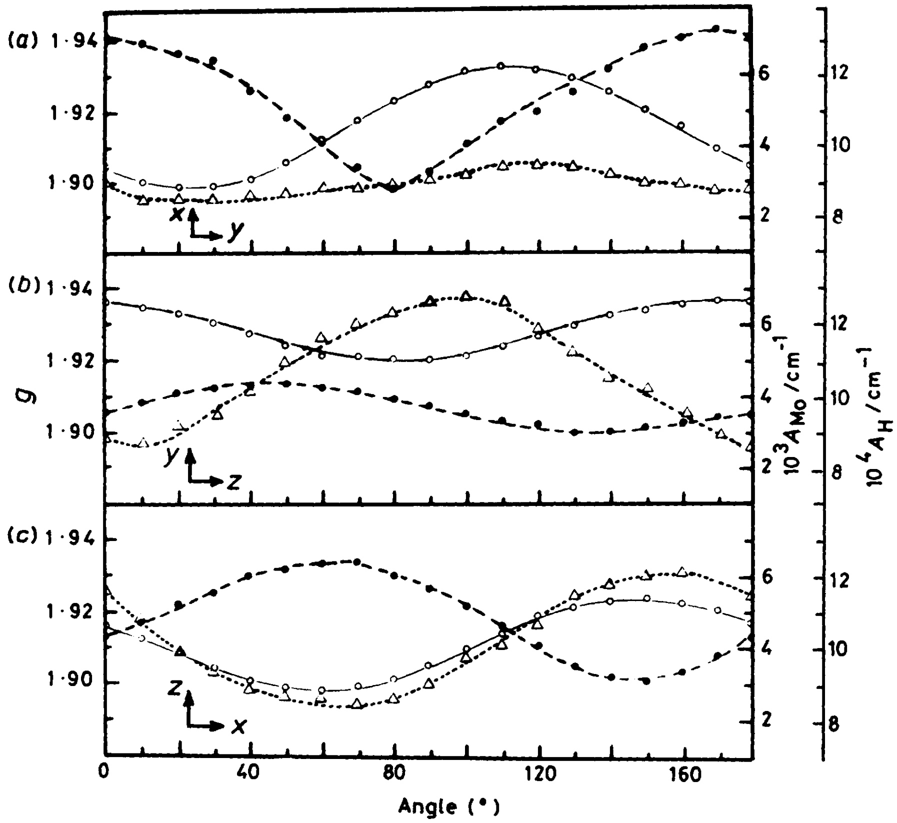

Figure 4. Angular variation of g (—O—), A_M (- - ● - -), and A_H (· · · △ · · ·) in the xy (a), yz (b), and zx (c) planes

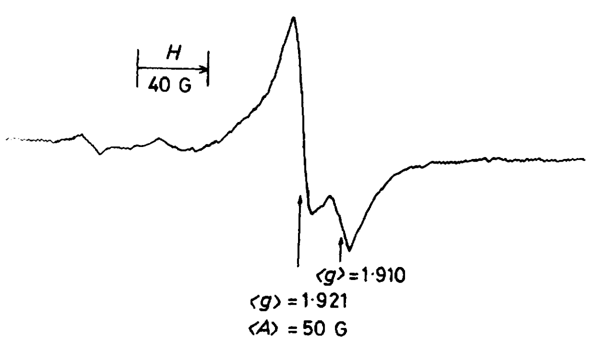

Figure 5. E.s.r. spectrum for the photolyte of the deaerated aqueous solution containing 13.6 mmol dm^{-3} $[NH_3Pr]_6[Mo_7O_{24}]\cdot 3H_2O$

good agreement with the average (g_0 = 1.919) of principal values of the g tensor for the Mo^V centre for the single crystal. The signs of the components for the A_{Mo} tensor in the Table are taken to be positive, as described for A_{Mo} parameters of various oxomolybdenum ions.[8] The non-coincidence of the principal axes of the g and A_{Mo} tensors, has its origin in mixing between the various metal-based antibonding molecular orbitals allowed by the low symmetry.[9]

To proceed we have to decide on a choice of signs for the components of experimental ^{1}H tensors. The decomposition into isotropic and anisotropic coupling constants for the ^{1}H superhyperfine coupling components gives us the different combinations of signs. The odd spin in the Mo^{V}OH fragment may be distributed in orbitals on the oxygen and molybdenum atoms. If the spin density on a molybdenum atom does not contribute to spin polarization of the OH bond, the coupling constant for H(O) is simply related to the spin density on the oxygen atom located in a 2p orbital and the known parameters of the $\dot{C}$H π-radical system enable us to estimate the spin density distribution.[10] Reasonable agreement with both sign and magnitude of this estimation may be obtained only with the choice of the same signs. Any other choice of signs results in an improbably high ratio (>2) of anisotropic and isotropic components,* since the principal values (B) of the anisotropic tensor found for an α-proton in a π-electron radical is within 70% of the isotropic hyperfine interaction (A_{iso}).[11] Thus, the tensors may now be broken up as shown below.

$$\begin{bmatrix} \pm\ 8.15 \\ \pm\ 9.14 \\ \pm 12.50 \end{bmatrix} \times 10^{-4}\,\text{cm}^{-1} = \left\{ \pm 9.93 + \begin{bmatrix} \mp 1.78 \\ \mp 0.79 \\ \pm 2.57 \end{bmatrix} \right\} \times 10^{-4}\,\text{cm}^{-1}$$

The OH bond has been assumed to be 40% ionic so that the spin density on the oxygen atom is taken to be A_{iso} (=9.93 × 10^{-4})/12.0 × 10^{-4} cm^{-1} = 0.8.[10,11] The value is unreasonably large, considering that the totality of the spin in this hypothesis is shared among the molybdenum, oxygen, and hydrogen atoms. Furthermore, applying the above hypothesis to the $Mo^VO_4(OH)_2$ centre in the $[Mo_8O_{26}(OH)_2]^{6-}$ lattice which gave similar ^{1}H superhyperfine principal values (±8.69, ±9.28, ±10.14) × 10^{-4} cm^{-1},[3] the total spin density is calculated to be unacceptably large, exceeding 0.8 × 2 = 1.6.

The result implies the possibility of the direct spin polarization between the paramagnetic electron orbital of molybdenum and the H orbital, which would produce positive spin

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* [$A_{H(1)}$, $A_{H(2)}$, $A_{H(3)}$] = (±8.15, ±9.14, ∓12.5), (±8.15, ∓9.14, ±12.5), and (∓8.15, ±9.14, ±12.5) × 10^{-4} cm^{-1} imply $|B|_{max.}/|A_{iso}|$ = 8.8, 3.4, and 2.7, respectively. These combinations constitute an unacceptably high ratio.

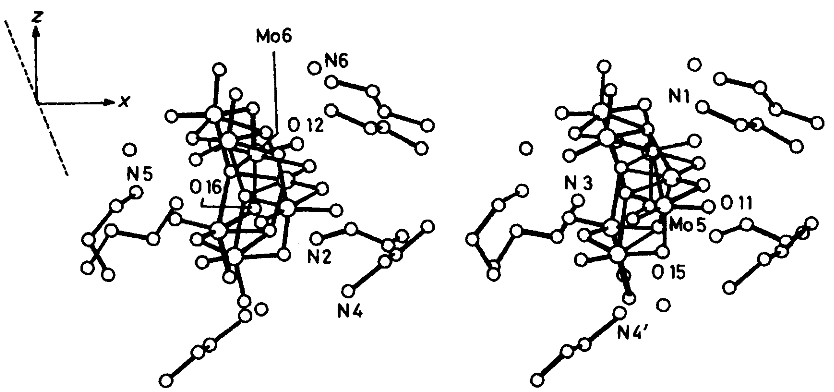
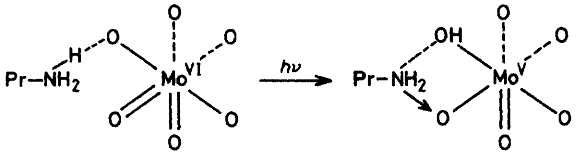


Figure 6. Stereoscopic drawing of the molecular structure looking down the y axis. Plausible H[O(16)] ··· Mo(6) direction corresponds to the dashed line on the zx plane

density at the proton. The hydrogen in this case is analogous to the β-hydrogen of a hydrocarbon free radical and such coupling components are definitely positive as shown in the Table.[10,12] The large isotropic H(O) value of 9.93×10^{-4} cm^{-1} strongly supports this possibility and yields a proton 1*s* contribution to the semi-occupied orbital of 0.02 which can be estimated from the isotropic hyperfine interaction (1 420 MHz = 474×10^{-4} cm^{-1}) for unit spin density in the 1*s* orbital of the H atom.[11,13] The coupling constants [*] respectively associated with a 5*s* and 4*d* orbital of ^{95,97}Mo are 1 984 MHz = 66.2×10^{-3} cm^{-1} and 150.7(2/7) [†] = 43.06 MHz = 1.44×10^{-3} cm^{-1}.[14] The isotropic coupling value for ^{95,97}Mo is 4.51×10^{-3} cm^{-1} (Table); hence a 5*s* contribution of 0.07 is indicated. For the ^{95,97}Mo(4*d*) contribution the anisotropic parameter can be estimated to be $(A_{Mo\parallel} - A_{Mo\perp})/3 = 1.24 \times 10^{-3}$ cm^{-1}, taking $A_{Mo\parallel} = 6.99 \times 10^{-3}$ cm^{-1} and $A_{Mo\perp} = [(4.20 + 2.34)/2] \times 10^{-3} = 3.27 \times 10^{-3}$ cm^{-1} (see Table).[14] Hence, ^{95,97}Mo(4*d*) orbitals contribute an estimated 0.86 to the semi-occupied orbital. The total spin count is thus 0.02 (H 1*s*) + 0.07 (Mo 5*s*) + 0.86 (Mo 4*d*) = 0.95, which is close to unity. This indicates that 4*d* orbitals appreciably contribute to the semi-occupied molecular orbital and that the direct spin polarization between the paramagnetic electron orbital of molybdenum and the H orbital is reasonably possible.

Accordingly, the maximum principal component $A_{H(3)}$ was expected to be nearly parallel to the H(O) ··· Mo^{V}, as well as the case of the $\dot{C}$OH system in which the hydroxyl-hydrogen maximum coupling was approximately parallel to a line H(O) ··· $\dot{C}$.[10,12] The plot of the angular dependence of the A_H values in the crystal yz plane gains its maximum (12.7×10^{-4} cm^{-1}) at *ca.* 5° from the z axis (Figure 4). The value almost approaches the highest of the principal A_H values, $A_{H(3)}$ (12.5×10^{-4} cm^{-1}). Furthermore, the relatively large A_H value (12.1×10^{-4} cm^{-1}) in the zx plane, at *ca.* 20° from the z axis, approaches $A_{H(3)}$, since $A_{H(3)}$ is nearly perpendicular to the y axis and is gained at 111.5 and 21.5° from the x and z axes, respectively (Table). Hence, these directions in the yz and zx planes were considered to be nearly coincident with the direction of the H(O) ··· Mo^{V}. Since $[NH_3Pr]_6[Mo_7O_{24}]\cdot 3H_2O$ is a photochromic compound and exhibits no significant change in the i.r. spectra and *X*-ray diffraction powder patterns after u.v.-irradiation,[6] it is assumed that the structure of the parent oxidized form $[Mo_7O_{24}]^{6-}$ is retained upon u.v.-irradiation. Thus the present e.s.r. results are in agreement with the site symmetry determined for $[NH_3Pr]_6[Mo_7O_{24}]\cdot 3H_2O$.[4] The stereodiagram of the molecular structure viewed down the y axis is shown in Figure 6. The Mo–O bonds for isopolymolybdates can be classified into four types by their bond distances: *a* (1.69—1.73), *b* (1.90—1.97), *c* (2.16—2.30), and *d* (2.46—2.55 Å).[4,15] From the results of *X*-ray analysis and e.s.r. studies for the $[NH_3Pr^i]_6[H_2Mo_8O_{28}]\cdot 2H_2O$ single crystal, it has been proposed that the photoreduction of Mo^{VI} to Mo^{V} proceeds *via* u.v.-induced charge transfer in an *a*-type terminal Mo=O bond with an accompanying transfer of a hydrogen-bonding proton (N^{+}–H distance of *ca.* 0.9 Å) from an alkylammonium nitrogen to a *b*-type bridging oxygen atom (the N ··· O distance of *ca.* 2.86 Å), followed by an interaction of the non-bonding electrons of the amino nitrogen with the terminal oxo-group leading to a charge-transfer complex (I) as shown in reaction (2).[3] Reaction (2) shows a photoreducible MoO_6 site, in which the Mo^{VI} atom is surrounded by a distorted octahedral set of six oxygen atoms, two (*a*-type) of which are of terminal doubly bonded dioxo-groups and four (*b*—*d*-types) which are bridging.[1,3] Based on the assumptions that the proton transferred at the photoreduced MoO_6 site is located around the N ··· O line and that such a O–H bond length [‡] is comparative to one third (*ca.* 1 Å) of the N ··· O distance, the $A_{H(3)}$ vector direction was matched with the plausible H(O) ···Mo^{V} direction using the stereodiagrams of the molecular structures viewed down the x, y, and z axes. The result indicates that the $A_{H(3)}$ direction is close to the H[O(16)] ··· Mo(6). Considering that the short distance (2.81 Å) [§] between N(2) and O(16) renders the postulated proton transfer from N(2) to a *b*-type O(16) (Mo–O 1.93 Å) eminently reasonable,[4] the H[O(16)] ··· Mo(6) direction postulated as a result of the proton transfer is observed at *ca.* 110 and 20° from the x and z axes in the zx plane, respectively (Figure 6). This direction is nearly coin-



(2)

(I)

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[*] Values of A and P in ref. 14 for ^{97}Mo can be estimated to be equivalent to those for ^{95}Mo because of an approximate equivalency of the absolute value of gyromagnetic ratio of the nucleus in question.

[†] (2/7) is the angular factor for *d* orbitals. See Table 2 in ref. 14.

[‡] The O–H distance may be taken as the same (0.9 Å) as the O–H distance for $[Mo_8O_{26}(OH)_2]^{6-}$.[3,15]

[§] The hydrogen bond distance of H[N(2)] ··· O(16) is *ca.* 2 Å.

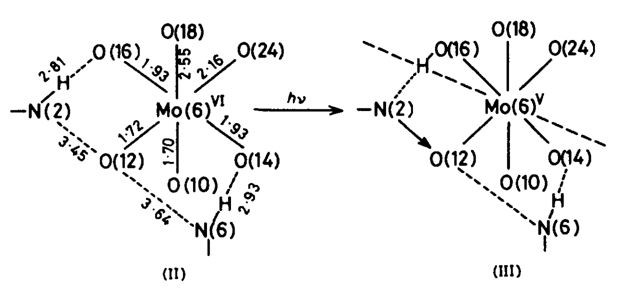

Figure 7. Bond distances (Å) in the environment of the Mo(6) site and the mode of the photoreaction. The large-dashed line represents the H[O(16)] · · · $Mo(6)^V$ direction which is nearly coincident with the $A_{H(3)}$ vector direction

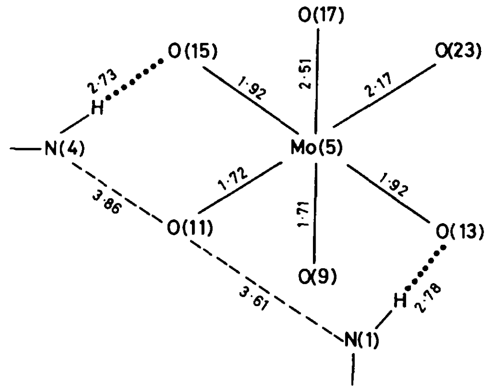

Figure 8. Environment of the Mo(5) site

cident with the $A_{H(3)}$ vector direction. Figure 7 shows the configuration (II)[4] about the environment of the Mo(6) site with the mode of the solid-state photoreaction given by the charge-transfer complex (III) formation. The long distance (2.93 Å) of N(6) · · · O(14) is a factor which decreases the probability of the proton transfer. This excludes the possibility of the H[O(14)] · · · Mo(6) direction as the $A_{H(3)}$ direction, which results from the proton transfer from N(6) to O(14).

Any other molybdenum site was not found to accord well with experimental data. The octahedron environment of the Mo(5) is similar to that of the Mo(6), as shown in Figure 8.[4] One should note the long distance (3.86 or 3.61 Å) between O(11) and N(4) or N(1) in the Mo(5) site, compared with the O(12) · · · N(2) distance (3.45 Å) in the Mo(6) site. Since the photoeffect is possibly to induce charge transfer (O→Mo) in an *a*-type terminal Mo=O bond, causing the oxygen to interact with the amino nitrogen as a result of the proton transfer,[1,3,4] the long distance in O(11) · · · N(4) or O(11) · · · N(1) may lead to a lowering in the probability of the charge-transfer complex (I) formation in the Mo(5) site, resulting in a relative insensitivity to the photoreduction of the Mo(5). Interesting, also, is the fact that for diperoxoheptamolybdate anion $[Mo_7O_{22}(O_2)_2]^{6-}$, two peroxo groups replace two *a*-type terminal oxygen atoms, one at either end [corresponding to Mo(6) or Mo(5) site] of $[Mo_7O_{24}]^{6-}$.[16]

Acknowledgements

I am grateful to Professor Y. Sasada and Dr. Y. Ohashi for affording facilities for the taking of the stereo-diagrams of the molecule in the crystal.

References

1 Part 5, T. Yamase, R. Sasaki, and T. Ikawa, *J. Chem. Soc., Dalton Trans.*, 1981, **628**.
2 T. Yamase and T. Ikawa, *Inorg. Chim. Acta*, 1979, **37**, L529; 1980, **45**, L55; T. Yamase, *ibid.*, 1981, **54**, L165.
3 T. Yamase, *J. Chem. Soc., Dalton Trans.*, 1978, 283.
4 Y. Ohashi, K. Yanagi, Y. Sasada, and T. Yamase, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1254.
5 H. T. Evans jun., B. M. Gatehouse, and P. Leverett, *J. Chem. Soc., Dalton Trans.*, 1975, 505.
6 T. Yamase and T. Ikawa, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 746.
7 M. Che, M. Fournier, and J. P. Launay, *J. Chem. Phys.*, 1979, **71**, 1954 and refs. therein.
8 B. R. McGarvey, *J. Phys. Chem.*, 1967, **71**, 51.
9 A. Abragam and H. M. L. Pryce, *Proc. Roy. Soc. London, Ser. A*, 1951, **205**, 135.
10 W. Derbyshire, *Mol. Phys.*, 1962, **5**, 225.
11 J. R. Morton, *Chem. Rev.*, 1964, **64**, 453.
12 D. Pooley and D. H. Whiffen, *Trans. Faraday Soc.*, 1961, **57**, 1445.
13 P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967, p. 24.
14 J. R. Morton and K. F. Preston, *J. Magn. Reson.*, 1978, **30**, 577.
15 M. Isobe, F. Marumo, T. Yamase, and T. Ikawa, *Acta Crystallogr., Sect. B*, 1978, **34**, 2728.
16 I. Larking and R. Stomberg, *Acta Chem. Scand.*, 1972, **26**, 3708.

Received 17*th February* 1982; *Paper* 2/293