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Characterization of a Weak Intermolecular Photosensitive Complex between an Organic Substrate and a Polyoxometalate. Crystal and Molecular Structure of α-$H_3PMo_{12}O_{40}\cdot6DMA\cdot CH_3CN\cdot0.5H_2O$ (DMA = *N,N*-Dimethylacetamide)

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A solvated complex, **1**, between the heteropolymolybdate α-$H_3PMo_{12}O_{40}$ and the substrate *N,N*-dimethylacetamide (DMA) with the stoichiometry α-$H_3PMo_{12}O_{40}\cdot6DMA$ has been isolated, purified and characterized. This yellow complex is highly photosensitive. Irradiation into the low-energy charge-transfer electronic spectral bands of **1** either in the crystalline form or in solution results in oxidation of the DMA substrate molecules and reduction of the polyoxometalate. The electronic spectra (λ 300–600 nm) as well as the ^1H NMR spectra for **1** dissolved in DMA and CD_3CN establish that this weak intermolecular complex dissociates into free $PMo_{12}O_{40}{}^{3-}$ and DMA moieties in solution unless the organic donor/substrate, DMA, is present in very high concentrations. The ^{31}P NMR and ^{17}O NMR spectra (22 atom % ^{17}O enriched) of **1** establish that there is no covalent modification of the Keggin polyoxometalate structure under conditions of full association of **1** in solution (100% DMA). Light- and desolvation-sensitive yellow prisms of **1** crystallize from acetonitrile as an acetonitrile aquo solvate of formula α-$H_3PMo_{12}O_{40}\cdot6DMA\cdot CH_3CN\cdot0.5H_2O$ in the monoclinic space group $P2_1/n$. The unit cell has $a = 13.595$ (6) Å, $b = 23.091$ (14) Å, $c = 21.040$ (7) Å, $\beta = 92.50$ (3)°, $V_{calcd} = 6598.45$ (5.2) Å^3, and $Z = 4$. The structure was solved by the heavy-atom method and refined to a final $R = 0.0529$ ($R_w = 0.0492$). The structure is remarkably free of disorder. The three polyoxometalate hydrogen atoms could not be located directly, but several structural features suggest strongly that they are associated with the six DMA solvate molecules as three strongly hydrogen bonded dimers, $[DMA\text{-}H\text{-}DMA]^+$. The acetonitrile and water molecules of crystallization and one of three DMA dimers are not within van der Waals distances of any part of the polyoxometalate. The four carbonyl oxygens and three of the four carbonyl carbons in the second and third DMA dimers are within van der Waals distance of the terminal oxo oxygens of the polyoxometalate.

Introduction

In the last few years there has been a rapidly growing number of reports in the literature addressing the use of polyoxometalates as both homogeneous[1-3] and heterogeneous catalysts.[4] A substantial portion of the reported homogeneous catalytic processes are photochemical in nature. The earliest systematic studies of polyoxometalate photochemistry involved aqueous solutions of alkylammonium isopolymolybdates and tungstates by Yamase and co-workers.[5] On the basis of radical trapping, single-crystal EPR, and other data these investigators reported that photoreduction of the isopolyoxometalates by water or organic substrates present in the aqueous solution involved initial generation of hydroxyl radicals by a photoexcited hydrogen-bonded complex between the cation and the polyanion followed by other processes. Later the catalytic photochemical oxidations, principally of alcohols, by a variety of polyoxomolybdates and -tungstates were investigated in some detail by the groups of Yamase,[6] Papaconstantinou,[7] Darwent,[8] and others[9] as well as our group.[10] It is clear from these investigations that a number of polyoxometalates of both the isopoly and heteropoly class are capable of catalyzing the photochemical dehydrogenation (eq 1) or air oxidation (eq 2) of

$$SH_2 \xrightarrow{P,\ h\nu} S + H_2 \qquad (1)$$

$$SH_2 + {}^1/{}_2O_2 \xrightarrow{P,\ h\nu} S + H_2O \qquad (2)$$

SH_2 = organic substrate = alcohol, amide, aldehyde,
ether, alkane, or one of many other organic functions;
P = polyoxometalate catalyst

a number of organic substrates. Under appropriate conditions, even saturated hydrocarbons can be functionalized.[11] The consensus based on more than one line of experimental evidence is that the substrate oxidation process in all these reactions involves electron transfer from the organic molecule to the polyoxometalate in a ligand-to-metal charge-transfer (LMCT) excited state. The most recent experimental observation testifying as to the complexity of the mechanisms of these catalytic photochemical organic oxidation reactions is that the spectroscopic and photochemical characteristics of some heteropoly complexes in 100% dipolar aprotic and certain other organic media constitute classical intermolecular electron donor–acceptor behavior.[10,12] We feel that the unequivocal characterization of photosensitive complexes

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between organic substrates and polyoxometalates in both the solid and solution states is of some importance in further elucidating many of the features of the catalytic photochemistry effected by polyoxometalates, such as that exemplified by eq 1 and 2. In accord with this we report here the isolation, purification, and several properties of a discrete photosensitive intermolecular complex between an organic substrate and a polyoxomolybdate, α-dodecamolybdophosphoric acid–6-(*N*,*N*-dimethylacetamide), α-$H_3PMo_{12}O_{40}$·6DMA (**1**).

Experimental Section

Materials. All organic solvents used for the physical measurements and syntheses were reagent grade or glass-distilled grade (Burdick and Jackson) and stored under argon. Deuteriated solvents were purchased from Aldrich. Isotopically enriched water (22 atom % ^{17}O) was purchased from Monsanto/DOE (Mound Facility, Miamisburg, OH). The precursor polyoxometalate, α-$H_3PMo_{12}O_{40}$·nH_2O, $n \approx 13$,[13] and α-$[n\text{-}Bu_4N]_3PMo_{12}O_{40}$[13,14] were prepared by literature methods. Elemental analyses were by either Atlanta Microlabs (for C, H, and N) or Galbraith Laboratories (for the other elements).

Physical Measurements. ^{31}P and ^{17}O NMR spectra were obtained with an IBM WP-200SY spectrometer operating at 81.01 and 27.13 MHz, respectively. ^1H NMR spectra were obtained with a Nicolet Model 360NB 360-MHz NMR spectrometer operating at 360.1 MHz. Infrared spectra of samples were obtained as KBr pellets (2–4 wt % sample in KBr) on a Perkin-Elmer Model 983 spectrophotometer. Electronic spectra (λ 300–600 nm) were recorded on a Hewlett-Packard Model 8451A multidiode array spectrometer. The crystallography is described below.

Preparation of α-Dodecamolybdophosphoric Acid-6-(*N*,*N*-Dimethylacetamide), α-$H_3PMo_{12}O_{40}$·6DMA (1). To a 30 mL Gooch crucible is added 10 mL of a 9.3 mM aqueous solution of α-$H_3PMo_{12}O_{40}$·nH_2O. To this stirred solution is added 2.0 mL (21.5 mmol) of DMA. The resulting precipitate is collected and then sucked as dry as possible on a fritted-glass funnel. *Care is taken to avoid all direct light in this and subsequent procedures as the product complex, **1**, is quite light-sensitive.* The precipitate is recrystallized three times from acetonitrile to yield 7.24 g of yellow crystals. ^1H NMR (Me_2SO-d_6; chemical shifts δ relative to Me_4Si internal standard): 5.17 (s, polyoxometalate, 3 H); 2.95 and 2.79 (s, two distinct *N*-methyl resonances due to hindered rotation, 18 H each); 1.96 (s, methyl adjacent to carbonyl, 18 H). ^{17}O NMR (chemical shifts δ relative to $H_2{}^{17}O$, DMA as solvent, conditions of full association of **1** in solution): 940.3 (terminal O); 586.5 (doubly bridging O); 547.2 (doubly bridging O); 347 (DMA O from natural-abundance ^{17}O). ^{17}O NMR (δ, CH_3CN as solvent, conditions of dissociation of **1** into free $PMo_{12}O_{40}{}^{3-}$ and DMA moieties in solution): 1103.7 (terminal O); 671.4 (doubly bridging O); 646.4 (doubly bridging O). The internal triply bridging oxygens of **1** were not specifically enriched by using ^{17}O-enriched H_3PO_4 in the preparation of the polyoxometalate precursor. As a consequence these oxygens did not contain enough ^{17}O for this resonance to be seen.[15] ^{31}P NMR (DMA; chemical shift δ relative to 85% orthophosphoric acid external standard): −0.95. This value was not corrected for bulk susceptibility. Results from elemental analyses were variable apparently due to the ready ability of the monoclinic form of crystalline **1** to occlude solvate molecules (see discussion of X-ray crystal structure below). Anal. Calcd for $C_{24}H_{57}Mo_{12}N_6O_{46}P$ ($H_3PMo_{12}O_{40}$·6DMA): C, 12.27; H, 2.45; Mo, 49.03; N, 3.58; P, 1.32. Calcd for $C_{26}H_{61}Mo_{12}N_7O_{46.5}P$ ($H_3PMo_{12}O_{40}$·6DMA·CH_3CN·0.5H_2O, the same stoichiometry in the particular crystal submitted for analysis by X-ray crystallography): C, 13.02; H, 2.60; Mo, 48.01; N, 4.09; P, 1.29. Found: C, 13.57; H, 2.53; Mo, 49.03; N, 4.26; P, 1.35.

X-ray Crystallography. Collection and Reduction of Intensity Data. A bright yellow prismatic crystal of **1** was coated with epoxy cement immediately after removal from the mother liquor in order to avoid crystal destruction by efflorescent desolvation. The crystal was then affixed to the end of a glass capillary and the capillary mounted on a goniometer head of a Syntex $P2_1$ four-circle diffractometer. Accurate cell dimensions were obtained by least-squares refinement of 19 centered reflections ($7.90 \leq 2\theta \leq 27.47°$; λ(Mo Kα) = 0.71069 Å). The ω Wyckoff scan method was used with a variable scan rate of 3.91–14.65° min^{-1} (scan/background = 1). Intensity measurements of 3 standards every 197 reflections showed no evidence of significant crystal deterioration. Intensities (2θ = 3–50°) were measured for 12612 reflections, of which 9135 unique reflections displayed $F_o \geq 3\sigma(F_o)$. Four reflections (−12,13,9; −2,4,6; 1,15,0; 0,1,3) were omitted and are believed to be in error due to their unusually large difference between F_c and F_o relative to the remaining reflections in the data set. Crystal and data collection parameters along with the values for the residuals after final refinement are summarized in Table I.

Table I. Crystallographic Data for α-Dodecamolybdophosphoric Acid–6-(*N*,*N*-Dimethylacetamide)–Acetonitrile–0.5-Water, α-$H_3PMo_{12}O_{40}$·6DMA·CH_3CN·0.5H_2O (**1**)

A. Crystal Data	
formula	$C_{26}H_{61}Mo_{12}N_7O_{46.5}P$
fw	2398.04
space group	monoclinic, $P2_1/n$ (No. 14)
systematic absences	$h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$; $h00$, $h = 2n + 1$; $00l$, $l = 2n + 1$
a, Å	13.595 (6)
b, Å	23.091 (14)
c, Å	21.040 (7)
β, deg	92.50 (3)
V, Å^3	6598.5 (5.2)
Z	4
D_{calcd}, g cm^{-3}	2.42
D_{obsd}, g cm^{-3}	2.46 (2)
cryst dimens, mm	0.4 × 0.58 × 0.4
color	bright yellow
habit	prismatic
μ(calcd), cm^{-1}	22.74
B. Data Collection	
diffractometer	Syntex (Nicolet) $P2_1$
radiation (monochromatic)	Mo Kα (λ = 0.71069 Å)
R(merge), *R*(σ)	0.0087, 0.0406
total reflecns measd	12612
unique reflecns collected/indep reflecns	11587/9135 ($F_o > 3\sigma(F_o)$)
scan method	ω (Wyckoff)
2θ range, deg	3–50
scan speed, deg min^{-1}	3.91–14.65
bkgd/scan time	1
reflecns measd	$+h,+k,\pm l$
temp, °C	20
C. Refinement	
abs corr	semiempirical (ψ-scan)
max, min transmission	0.366, 0.320
max residual electron density, e Å^{-3}	1.45 (1.21 Å from Nd)
R^a	0.0529
$R_w{}^b$	0.0492
GOF^c	1.659

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]$. [c] GOF (goodness of fit) = $[\sum w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o is the number of observations, n_v is the number of parameters, and $w^{-1} = (\sigma^2(F) + |0.0002|F^2)$.

Structure Solution and Refinement. The computer hardware and software for data refinement and structure solution were described previously.[16] The data exhibited the following systematic absences: hkl; $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$; $h00$, $h = 2n + 1$; $00l$, $l = 2n + 1$. The monoclinic space group was uniquely determined to be $P2_1/n$ (nonstandard setting of $P2_1/c$ (No. 14)). Conventional Patterson synthesis provided positions for most of the Mo atoms. Subsequent Fourier syntheses and least-squares refinement provided locations for the remaining non-hydrogen atoms. Hydrogen positions were not readily discernible from electron density difference maps. Methyl hydrogens were placed in their calculated positions and were allowed to "ride" on their parent carbon atoms (C–H = 0.96 Å; $U_{iso}(H) = 1.2[U_{eq}(C)]$). All non-hydrogen atoms were refined anisotropically. The final electron density difference map was featureless with the maximum positive peak 1.45 e Å^{-3} at a distance of 1.21 Å from N(d) of DMA molecule d. Blocked-cascade least-squares refinement of 838 variables gave final agreement factors of $R = 0.0529$, $R_w = 0.0492$, and GOF = 1.659 (see Table I for definitions of R, R_w, and GOF). On the last cycle of the

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Table II. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$)

atom	x	y	z	U^a	atom	x	y	z	U^a
P	4923 (1)	6512 (1)	7102 (1)	22 (1)	O(10d)	2158 (4)	6818 (2)	6604 (3)	37 (2)
Mo(1)	6822 (1)	7004 (1)	6140 (1)	39 (1)	O(10e)	1855 (4)	7824 (3)	7266 (3)	50 (2)
Mo(2)	7122 (1)	7015 (1)	7890 (1)	38 (1)	O(10f)	2373 (4)	6787 (2)	7854 (3)	40 (2)
Mo(3)	7034 (1)	5627 (1)	7019 (1)	33 (1)	O(11e)	2163 (4)	5763 (3)	8517 (3)	54 (2)
Mo(4)	4833 (1)	7873 (1)	6314 (1)	40 (1)	O(11f)	2289 (4)	5811 (2)	7200 (3)	38 (2)
Mo(5)	5004 (1)	7774 (1)	8067 (1)	37 (1)	O(12e)	1721 (4)	5810 (3)	5922 (3)	50 (2)
Mo(6)	5303 (1)	6449 (1)	8772 (1)	39 (1)	Oa	4928 (6)	7185 (4)	11008 (4)	88 (4)
Mo(7)	5079 (1)	5116 (1)	7816 (1)	39 (1)	Na	6098 (6)	7449 (4)	10365 (4)	59 (3)
Mo(8)	4939 (1)	5216 (1)	6196 (1)	37 (1)	C(1a)	5726 (7)	7085 (4)	10768 (4)	51 (3)
Mo(9)	4616 (1)	6639 (1)	5423 (1)	42 (1)	C(2a)	6295 (9)	6554 (4)	10931 (5)	77 (5)
Mo(10)	2732 (1)	7327 (1)	7192 (1)	36 (1)	C(3a)	7038 (8)	7406 (5)	10082 (6)	84 (5)
Mo(11)	2918 (1)	6054 (1)	8007 (1)	38 (1)	C(4a)	5517 (10)	7968 (5)	10197 (5)	86 (5)
Mo(12)	2661 (1)	6044 (1)	6390 (1)	34 (1)	Ob	6010 (5)	411 (3)	1322 (3)	62 (3)
O(1a)	7861 (4)	7181 (3)	5801 (3)	52 (2)	Nb	6884 (6)	702 (3)	2175 (4)	50 (3)
O(1b)	7050 (4)	6244 (2)	6383 (3)	36 (2)	C(1b)	6104 (7)	460 (4)	1914 (5)	49 (3)
O(1c)	7128 (4)	7193 (2)	7024 (3)	40 (2)	C(2b)	5358 (9)	229 (6)	2325 (6)	101 (6)
O(1d)	6031 (4)	6791 (2)	5424 (3)	43 (2)	C(3b)	7086 (9)	764 (5)	2861 (5)	78 (5)
O(1e)	6138 (4)	7753 (2)	6108 (3)	40 (2)	C(4b)	7612 (8)	951 (5)	1774 (5)	76 (5)
O(1f)	5191 (4)	6856 (2)	6506 (2)	31 (2)	Oc	6079 (6)	8644 (3)	4765 (4)	80 (3)
O(2a)	8264 (4)	7182 (3)	8152 (3)	56 (2)	Nc	6697 (7)	7846 (4)	4352 (4)	72 (4)
O(2c)	7260 (4)	6211 (2)	7604 (3)	35 (2)	C(1c)	6787 (10)	8317 (4)	4682 (5)	65 (4)
O(2d)	6439 (4)	7684 (2)	8087 (3)	38 (2)	C(2c)	7734 (10)	8455 (5)	4960 (6)	92 (6)
O(2e)	6606 (4)	6664 (2)	8653 (3)	38 (2)	C(3c)	7457 (12)	7441 (5)	4228 (6)	122 (8)
O(2f)	5381 (4)	6807 (2)	7688 (2)	29 (2)	C(4c)	5736 (11)	7725 (6)	4048 (7)	119 (7)
O(3a)	8136 (4)	5331 (3)	6947 (3)	47 (2)	Od	4776 (6)	−179 (4)	768 (4)	94 (4)
O(3d)	6468 (4)	5130 (2)	7609 (3)	36 (2)	Nd	3363 (7)	−364 (4)	269 (4)	69 (4)
O(3e)	6298 (4)	5187 (2)	6361 (3)	36 (2)	C(1d)	3905 (7)	8 (4)	591 (4)	47 (3)
O(3f)	5316 (4)	5894 (2)	7057 (2)	29 (2)	C(2d)	3669 (13)	577 (5)	719 (6)	138 (9)
O(4c)	5157 (4)	7972 (2)	7171 (3)	38 (2)	C(3d)	2404 (7)	−273 (5)	18 (4)	64 (4)
O(4d)	4458 (4)	7434 (2)	5548 (3)	42 (2)	C(4d)	3776 (11)	−952 (5)	147 (6)	111 (7)
O(4e)	4624 (5)	8546 (3)	6061 (3)	55 (2)	Oe	3529 (7)	512 (3)	4599 (4)	99 (4)
O(4f)	3539 (4)	7659 (2)	6594 (3)	35 (2)	Ne	3435 (7)	−429 (4)	4434 (4)	66 (4)
O(5d)	4926 (5)	8425 (3)	8406 (3)	55 (2)	C(1e)	3619 (8)	13 (4)	4813 (5)	60 (4)
O(5e)	5005 (4)	7280 (2)	8771 (3)	39 (2)	C(2e)	3866 (9)	−86 (5)	5498 (5)	76 (5)
O(5f)	3713 (4)	7598 (2)	7823 (2)	36 (2)	C(3e)	3510 (9)	−1041 (4)	4610 (6)	88 (5)
O(6c)	3433 (4)	6462 (2)	5779 (3)	38 (2)	C(4e)	3114 (11)	−308 (6)	3751 (5)	112 (7)
O(6e)	5314 (5)	6329 (3)	9558 (3)	55 (2)	Of	6300 (7)	3376 (4)	8429 (4)	113 (4)
O(6f)	3925 (4)	6363 (2)	8532 (3)	38 (2)	Nf	6855 (7)	3657 (4)	7508 (5)	74 (4)
O(7d)	5070 (5)	4529 (2)	8274 (3)	52 (2)	C(1f)	6184 (8)	3433 (4)	7835 (5)	57 (4)
O(7e)	4829 (4)	4800 (2)	7010 (3)	40 (2)	C(2f)	5308 (9)	3243 (6)	7524 (10)	170 (11)
O(7f)	3828 (4)	5417 (2)	7868 (3)	37 (2)	C(3f)	6857 (12)	3749 (5)	6854 (6)	125 (8)
O(8c)	4993 (4)	5853 (2)	5667 (3)	36 (2)	C(4f)	7757 (10)	3843 (6)	7880 (9)	155 (10)
O(8e)	4765 (5)	4660 (3)	5698 (3)	53 (2)	C(1s)	5247 (10)	1543 (7)	8044 (8)	122 (8)
O(8f)	3586 (4)	5461 (2)	6330 (3)	36 (2)	C(2s)	5150 (8)	1301 (6)	7411 (8)	91 (6)
O(9d)	4361 (5)	6576 (3)	4648 (3)	58 (3)	Ns	5037 (9)	1102 (6)	6941 (6)	132 (7)
O(9f)	5464 (4)	5714 (2)	8428 (3)	37 (2)	Ow	9296 (19)	−12 (7)	4904 (12)	181 (15)
O(10a)	3812 (4)	6496 (2)	7144 (2)	28 (2)					

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

least-squares refinement the ratio of the maximum shift to the estimated standard deviation was 0.084. The data were corrected for absorption by semiempirical (ψ-scan) methods.[17] A weighting scheme utilizing weights of the form $w = [\sigma^2(F) + |g|F^2]^{-1}$ (where $g = 0.0002$) was implemented. Scattering factors were those used for neutral atoms.[18] The final positional and thermal parameters are given in Table II.

Results and Discussion

Synthesis, Electronic Structure, and Stability of 1 in Solution. When concentrated aqueous solutions of the amide substrate *N,N*-dimethylacetamide (DMA) and the heteropolymolybdate α-$H_3PMo_{12}O_{40}\cdot nH_2O$ are mixed, a new material far less soluble in water than either of the components precipitates from solution. This complex between the heteropolyacid and the organic substrate, α-$H_3PMo_{12}O_{40}\cdot 6DMA$ (**1**), can be recrystallized from acetonitrile to yield yellow prisms. Similarly colored isolable photosensitive intermolecular complexes form between other heteropolymolybdates or -tungstates and a number of electron-rich organic substrates.

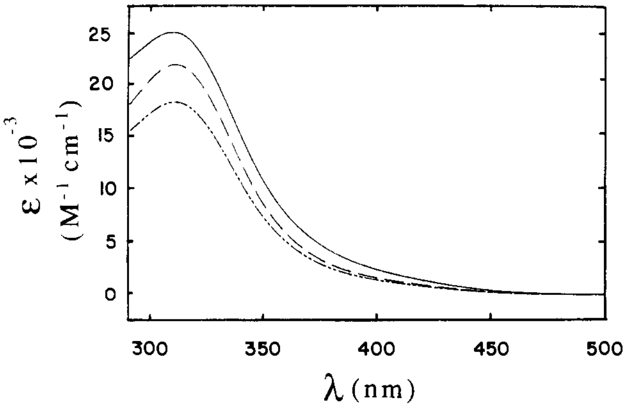

Figure 1. Comparison of the electronic spectra of three discrete forms of the α-$PMo_{12}O_{40}^{3-}$ moiety in solution showing the region with the charge-transfer maxima: (– –) α-$H_3PMo_{12}O_{40}\cdot 6DMA$ (**1**) in CH_3CN; (—) **1** in DMA; (–·–·–) $(n\text{-}Bu_4N)_3PMo_{12}O_{40}$ in CH_3CN. All spectra were obtained on 0.46 mM solutions in 0.1-cm cells at 24 °C.

Whereas the common aquated forms of heteropoly acids display no detectable photochemistry in the near-UV or visible region of the spectrum where they absorb and the quaternary ammonium forms of heteropoly compounds display negligible or very low levels of photochemistry in this region, the situation with respect to **1** is quite different. This complex is highly photosensitive in the

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(17) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

(18) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

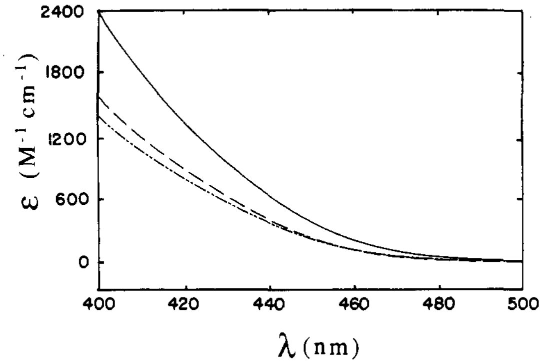

Figure 2. Solvent effects on the absorption tail of α-$PMo_{12}O_{40}^{3-}$: (--) 1 in CH_3CN; (—) 1 in DMA; (---) $(n\text{-}Bu_4N)_3PMo_{12}O_{40}$ in CH_3CN. All spectra were obtained on 0.46 mM solutions in 1.0-cm cells at 24 °C.

near-UV or visible region where it absorbs (Figures 1 and 2) either in solution or in the crystalline form analyzed by X-ray crystallography (vide infra). Manipulations involving **1** must be carried out in a darkened laboratory. Furthermore, irradiation of **1** results in a well-defined photoredox process in which the DMA molecules are oxidized and the polyoxometalate is reduced. The organic chemistry resulting from the oxidized DMA moieties is complicated and will be addressed in complete mechanistic studies to be published subsequently.

The electronic spectra of either α-$H_3PMo_{12}O_{40}\cdot nH_2O$ or **1** dissolved in a weakly coordinating solvent such as acetonitrile in the absence and presence of DMA clearly indicate that the DMA–polyoxometalate intermolecular interactions are weak and are almost entirely disrupted unless the mole fraction of DMA in the acetonitrile solvent approaches 1.0. Crystalline **1** dissociates extensively into α-$H_3PMo_{12}O_{40}$ and free DMA molecules when dissolved at millimolar concentrations in acetonitrile (Figures 1 and 2). Indeed, the purification of **1** by recrystallization from acetonitrile results in initial breakage followed by complete reformation of the weak intermolecular DMA–polyoxometalate interactions in the complex. The ^1H, ^{17}O, and ^{31}P NMR spectra taken of **1** in acetonitrile vs. those spectra taken in DMA confirm this behavior. The ^1H NMR spectrum of crystalline **1** dissolved in acetonitrile shows minimally perturbed freely diffusing DMA molecules. The ^{31}P NMR spectra of α-$PMo_{12}O_{40}^{3-}$ species do not have chemical shifts that vary appreciably with medium and consequently yield little or no information regarding the intermolecular DMA–polyoxometalate interactions. Figures 1 and 2 clearly show the effect of the DMA molecules on the complex charge-transfer absorption manifold of α-$H_3PMo_{12}O_{40}$ when the organic molecules are in the primary solvation sphere of the heteropolyacid. The presence of the DMA molecules results in a noticeable hyperchromic and slight bathochromic shift of the electronic absorption spectrum of the α-$PMo_{12}O_{40}^{3-}$ species. This shift parallels the shift of the photochemical action spectrum for α-$PMo_{12}O_{40}^{3-}$ reduction and DMA oxidation. The shifts in the absorption and action spectra of α-$H_3PMo_{12}O_{40}$ induced by DMA are far less dramatic than those shifts induced in heteropolyacids of molybdenum and tungsten by some other organic substrates.

Table III. Bond Lengths (Å)

P–O(1f)	1.542 (5)	P–O(2f)	1.519 (5)
P–O(3f)	1.528 (5)	P–O(10a)	1.516 (5)
Mo(1)–O(1a)	1.662 (6)	Mo(1)–O(1b)	1.849 (5)
Mo(1)–O(1c)	1.939 (6)	Mo(1)–O(1d)	1.878 (6)
Mo(1)–O(1e)	1.964 (5)	Mo(1)–O(1f)	2.404 (5)
Mo(2)–O(1c)	1.867 (6)	Mo(2)–O(2a)	1.670 (6)
Mo(2)–O(2c)	1.963 (5)	Mo(2)–O(2d)	1.859 (5)
Mo(2)–O(2e)	1.956 (6)	Mo(2)–O(2f)	2.434 (5)
Mo(3)–O(1b)	1.956 (5)	Mo(3)–O(2c)	1.842 (5)
Mo(3)–O(3a)	1.660 (6)	Mo(3)–O(3d)	1.879 (5)
Mo(3)–O(3e)	1.958 (5)	Mo(3)–O(3f)	2.420 (5)
Mo(4)–O(1e)	1.865 (6)	Mo(4)–O(1f)	2.428 (5)
Mo(4)–O(4c)	1.851 (5)	Mo(4)–O(4d)	1.953 (6)
Mo(4)–O(4e)	1.664 (6)	Mo(4)–O(4f)	1.943 (5)
Mo(5)–O(2d)	1.961 (6)	Mo(5)–O(2f)	2.433 (5)
Mo(5)–O(4c)	1.961 (6)	Mo(5)–O(5d)	1.670 (6)
Mo(5)–O(5e)	1.869 (5)	Mo(5)–O(5f)	1.852 (5)
Mo(6)–O(2e)	1.868 (6)	Mo(6)–O(2f)	2.432 (5)
Mo(6)–O(5e)	1.963 (6)	Mo(6)–O(6e)	1.676 (6)
Mo(6)–O(6f)	1.929 (6)	Mo(6)–O(9f)	1.860 (5)
Mo(7)–O(3d)	1.957 (6)	Mo(7)–O(3f)	2.433 (5)
Mo(7)–O(7d)	1.665 (6)	Mo(7)–O(7e)	1.864 (6)
Mo(7)–O(7f)	1.845 (6)	Mo(7)–O(9f)	1.944 (5)
Mo(8)–O(3e)	1.866 (6)	Mo(8)–O(3f)	2.432 (5)
Mo(8)–O(7e)	1.974 (6)	Mo(8)–O(8c)	1.849 (6)
Mo(8)–O(8e)	1.667 (6)	Mo(8)–O(8f)	1.956 (5)
Mo(9)–O(1d)	1.955 (6)	Mo(9)–O(1f)	2.429 (5)
Mo(9)–O(4d)	1.869 (6)	Mo(9)–O(6c)	1.848 (6)
Mo(9)–O(8c)	1.947 (6)	Mo(9)–O(9d)	1.658 (6)
Mo(10)–O(4f)	1.870 (5)	Mo(10)–O(5f)	1.943 (5)
Mo(10)–O(10a)	2.422 (5)	Mo(10)–O(10d)	1.854 (5)
Mo(10)–O(10e)	1.667 (6)	Mo(10)–O(10f)	1.948 (6)
Mo(11)–O(6f)	1.862 (5)	Mo(11)–O(7f)	1.952 (6)
Mo(11)–O(10a)	2.452 (5)	Mo(11)–O(10f)	1.870 (6)
Mo(11)–O(11e)	1.658 (6)	Mo(11)–O(11f)	1.951 (5)
Mo(12)–O(6c)	1.952 (6)	Mo(12)–O(8f)	1.850 (5)
Mo(12)–O(10a)	2.416 (5)	Mo(12)–O(10d)	1.974 (5)
Mo(12)–O(11f)	1.877 (6)	Mo(12)–O(12e)	1.669 (6)
Oa–C(1a)	1.237 (13)	Na–C(1a)	1.312 (13)
Na–C(3a)	1.437 (14)	Na–C(4a)	1.469 (14)
C(1a)–C(2a)	1.482 (14)	Ob–C(1b)	1.252 (13)
Nb–C(1b)	1.300 (12)	Nb–C(3b)	1.464 (12)
Nb–C(4b)	1.448 (14)	C(1b)–C(2b)	1.461 (16)
Oc–C(1c)	1.242 (15)	Nc–C(1c)	1.294 (13)
Nc–C(3c)	1.426 (17)	Nc–C(4c)	1.456 (17)
C(1c)–C(2c)	1.427 (18)	Od–C(1d)	1.299 (12)
Nd–C(1d)	1.303 (13)	Nd–C(3d)	1.401 (13)
Nd–C(4d)	1.495 (16)	C(1d)–C(2d)	1.381 (16)
Oe–C(1e)	1.240 (13)	Ne–C(1e)	1.315 (13)
Ne–C(3e)	1.463 (14)	Ne–C(4e)	1.509 (14)
C(1e)–C(2e)	1.484 (14)	Of–C(1f)	1.261 (14)
Nf–C(1f)	1.275 (14)	Nf–C(3f)	1.392 (16)
Nf–C(4f)	1.488 (17)	C(1f)–C(2f)	1.404 (18)
C(1s)–C(2s)	1.446 (23)	C(2s)–Ns	1.095 (21)

X-ray Crystal Structure of 1. Diffraction-quality crystals of **1** can be grown from acetonitrile solution in the dark. In the monoclinic crystalline modification of **1** examined here, this intermolecular complex crystallizes as an acetonitrile aquo solvate of formula α-$H_3PMo_{12}O_{40}\cdot 6DMA\cdot CH_3CN\cdot 0.5H_2O$; the entire formula is in the asymmetric unit. A combined ORTEP plot and numbering diagram of all the non-hydrogen atoms in the asymmetric unit is given in Figure 3; selected bond distances and angles are given in Tables III and IV, respectively. A stereoview of the packing diagram (Figure S4) and an ORTEP plot of the DMAa-DMAf dimer interacting with adjacent polyoxometalates (Figure S5) are included in the supplementary material. All non-hydrogen atoms of the polyoxomolybdate as well as those of the eight solvate molecules are shown in Figure 3. Despite the relatively high quality of the data set, the presence of numerous heavy atoms in the structure precludes determination of the hydrogen atom positions. The acetonitrile and water molecules of crystallization are not within van der Waals distance of any polyoxometalate or DMA atoms.[19] On the basis of bond lengths, the six DMA molecules clearly are present as three protonated dimers (O–H···O hydrogen-bonded pairs) in the crystal structure (DMAa-DMAf, DMAb-DMAd, and DMAc-DMAe).[20] This pairing of the DMA molecules is fairly evident from Figure 3. These DMA pairs can be viewed as weakly binding the polyoxometalate molecules together, or equally apt, the polyoxometalate molecules can be viewed as weakly binding the DMA dimers together, resulting in a quite complex packing arrangement in the unit cell. All the bond distances and angles in the $PMo_{12}O_{40}^{3-}$ heteropolyanion are

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(19) There is half of a water molecule in the asymmetric unit, and the water molecule exhibits 50% occupancy in each of two symmetry-related proximal sites (separated by 1.940 Å) in the unit cell.

(20) The O–H···O distances, 2.458 Å for DMAa-DMAf, 2.420 Å for DMAb-DMAd, and 2.411 Å for DMAc-DMAe, are compatible with strong hydrogen bonds (the lower case letters a–f designate the atoms of DMA molecules a–f, respectively): Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91.

Table IV. Bond Angles (deg)

O(1f)–P–O(2f)	109.0 (3)	O(1f)–P–O(3f)	109.6 (3)	O(1d)–Mo(9)–O(9d)	100.3 (3)	O(1f)–Mo(9)–O(9d)	170.1 (3)
O(2f)–P–O(3f)	109.7 (3)	O(1f)–P–O(10a)	109.3 (3)	O(4d)–Mo(9)–O(9d)	101.7 (3)	O(6c)–Mo(9)–O(9d)	103.3 (3)
O(2f)–P–O(10a)	109.8 (3)	O(3f)–P–O(10a)	109.5 (3)	O(8c)–Mo(9)–O(9d)	102.7 (3)	O(4f)–Mo(10)–O(5f)	85.5 (2)
O(1a)–Mo(1)–O(1b)	102.6 (3)	O(1a)–Mo(1)–O(1c)	101.9 (3)	O(4f)–Mo(10)–O(10a)	85.5 (2)	O(5f)–Mo(10)–O(10a)	83.3 (2)
O(1b)–Mo(1)–O(1c)	85.5 (2)	O(1a)–Mo(1)–O(1d)	100.8 (3)	O(4f)–Mo(10)–O(10d)	93.0 (2)	O(5f)–Mo(10)–O(10d)	156.3 (2)
O(1b)–Mo(1)–O(1d)	93.3 (2)	O(1c)–Mo(1)–O(1d)	156.9 (3)	O(10a)–Mo(10)–O(10d)	73.0 (2)	O(4f)–Mo(10)–O(10e)	102.9 (3)
O(1a)–Mo(1)–O(1e)	100.2 (3)	O(1b)–Mo(1)–O(1e)	156.7 (2)	O(5f)–Mo(10)–O(10e)	100.8 (3)	O(10a)–Mo(10)–O(10e)	170.8 (2)
O(1c)–Mo(1)–O(1e)	85.2 (2)	O(1d)–Mo(1)–O(1e)	87.1 (2)	O(10d)–Mo(10)–O(10e)	102.5 (3)	O(4f)–Mo(10)–O(10f)	156.4 (2)
O(1a)–Mo(1)–O(1f)	170.5 (2)	O(1b)–Mo(1)–O(1f)	85.6 (2)	O(5f)–Mo(10)–O(10f)	84.4 (2)	O(10a)–Mo(10)–O(10f)	72.1 (2)
O(1c)–Mo(1)–O(1f)	83.5 (2)	O(1d)–Mo(1)–O(1f)	73.5 (2)	O(10d)–Mo(10)–O(10f)	87.7 (2)	O(10e)–Mo(10)–O(10f)	99.9 (3)
O(1e)–Mo(1)–O(1f)	72.2 (2)	O(1c)–Mo(2)–O(2a)	103.2 (3)	O(6f)–Mo(11)–O(7f)	85.6 (2)	O(6f)–Mo(11)–O(10a)	84.5 (2)
O(1c)–Mo(2)–O(2c)	84.5 (2)	O(2a)–Mo(2)–O(2c)	102.7 (3)	O(7f)–Mo(11)–O(10a)	82.2 (2)	O(6f)–Mo(11)–O(10f)	91.8 (2)
O(1c)–Mo(2)–O(2d)	93.3 (2)	O(2a)–Mo(2)–O(2d)	101.5 (3)	O(7f)–Mo(11)–O(10f)	154.8 (2)	O(10a)–Mo(11)–O(10f)	72.6 (2)
O(2c)–Mo(2)–O(2d)	155.5 (2)	O(1c)–Mo(2)–O(2e)	155.3 (2)	O(6f)–Mo(11)–O(11e)	103.4 (3)	O(7f)–Mo(11)–O(11e)	101.9 (3)
O(2a)–Mo(2)–O(2e)	100.7 (3)	O(2c)–Mo(2)–O(2e)	84.4 (2)	O(10a)–Mo(11)–O(11e)	171.3 (2)	O(10f)–Mo(11)–O(11e)	103.1 (3)
O(2d)–Mo(2)–O(2e)	87.8 (2)	O(1c)–Mo(2)–O(2f)	85.3 (2)	O(6f)–Mo(11)–O(11f)	155.4 (2)	O(7f)–Mo(11)–O(11f)	84.8 (2)
O(2a)–Mo(2)–O(2f)	170.4 (3)	O(2c)–Mo(2)–O(2f)	82.3 (2)	O(10a)–Mo(11)–O(11f)	71.8 (2)	O(10f)–Mo(11)–O(11f)	87.4 (2)
O(2d)–Mo(2)–O(2f)	73.2 (2)	O(2e)–Mo(2)–O(2f)	71.4 (2)	O(11e)–Mo(11)–O(11f)	100.7 (3)	O(6c)–Mo(12)–O(8f)	85.9 (2)
O(1b)–Mo(3)–O(2c)	85.3 (2)	O(1b)–Mo(3)–O(3a)	101.5 (3)	O(6c)–Mo(12)–O(10a)	82.4 (2)	O(8f)–Mo(12)–O(10a)	86.4 (2)
O(2c)–Mo(3)–O(3a)	103.7 (3)	O(1b)–Mo(3)–O(3d)	156.1 (2)	O(6c)–Mo(12)–O(10d)	84.4 (2)	O(8f)–Mo(12)–O(10d)	156.6 (2)
O(2c)–Mo(3)–O(3d)	93.9 (2)	O(3a)–Mo(3)–O(3d)	101.9 (3)	O(10a)–Mo(12)–O(10d)	71.3 (2)	O(6c)–Mo(12)–O(11f)	156.1 (2)
O(1b)–Mo(3)–O(3e)	85.1 (2)	O(2c)–Mo(3)–O(3e)	156.6 (2)	O(8f)–Mo(12)–O(11f)	93.7 (2)	O(10a)–Mo(12)–O(11f)	73.8 (2)
O(3a)–Mo(3)–O(3e)	99.0 (3)	O(3d)–Mo(3)–O(3e)	86.5 (2)	O(10d)–Mo(12)–O(11f)	86.8 (2)	O(6c)–Mo(12)–O(12e)	101.0 (3)
O(1b)–Mo(3)–O(3f)	82.9 (2)	O(2c)–Mo(3)–O(3f)	85.7 (2)	O(8f)–Mo(12)–O(12e)	103.3 (3)	O(10a)–Mo(12)–O(12e)	169.9 (2)
O(3a)–Mo(3)–O(3f)	169.8 (2)	O(3d)–Mo(3)–O(3f)	73.2 (2)	O(10d)–Mo(12)–O(12e)	99.4 (3)	O(11f)–Mo(12)–O(12e)	102.4 (3)
O(3e)–Mo(3)–O(3f)	72.0 (2)	O(1e)–Mo(4)–O(1f)	73.1 (2)	Mo(1)–O(1b)–Mo(3)	150.9 (3)	Mo(1)–O(1c)–Mo(2)	151.3 (3)
O(1e)–Mo(4)–O(4c)	93.3 (2)	O(1f)–Mo(4)–O(4c)	85.5 (2)	Mo(1)–O(1d)–Mo(9)	125.2 (3)	Mo(1)–O(1e)–Mo(4)	125.2 (3)
O(1e)–Mo(4)–O(4d)	87.0 (2)	O(1f)–Mo(4)–O(4d)	71.3 (2)	P–O(1f)–Mo(1)	126.0 (3)	P–O(1f)–Mo(4)	125.5 (3)
O(4c)–Mo(4)–O(4d)	155.6 (2)	O(1e)–Mo(4)–O(4e)	102.4 (3)	Mo(1)–O(1f)–Mo(4)	89.4 (2)	P–O(1f)–Mo(9)	125.4 (3)
O(1f)–Mo(4)–O(4e)	170.8 (3)	O(4c)–Mo(4)–O(4e)	103.0 (3)	Mo(1)–O(1f)–Mo(9)	89.5 (2)	Mo(4)–O(1f)–Mo(9)	89.4 (2)
O(4d)–Mo(4)–O(4e)	100.7 (3)	O(1e)–Mo(4)–O(4f)	156.3 (2)	Mo(2)–O(2c)–Mo(3)	151.8 (3)	Mo(2)–O(2d)–Mo(5)	126.1 (3)
O(1f)–Mo(4)–O(4f)	83.2 (2)	O(4c)–Mo(4)–O(4f)	85.2 (2)	Mo(2)–O(2e)–Mo(6)	126.6 (3)	P–O(2f)–Mo(2)	126.3 (3)
O(4d)–Mo(4)–O(4f)	84.9 (2)	O(4e)–Mo(4)–O(4f)	100.9 (3)	P–O(2f)–Mo(5)	126.4 (3)	Mo(2)–O(2f)–Mo(5)	88.8 (2)
O(2d)–Mo(5)–O(2f)	71.7 (2)	O(2d)–Mo(5)–O(4c)	84.1 (2)	P–O(2f)–Mo(6)	125.1 (3)	Mo(2)–O(2f)–Mo(6)	89.2 (2)
O(2f)–Mo(5)–O(4c)	82.3 (2)	O(2d)–Mo(5)–O(5d)	99.7 (3)	Mo(5)–O(2f)–Mo(6)	89.2 (2)	Mo(3)–O(3d)–Mo(7)	125.7 (3)
O(2f)–Mo(5)–O(5d)	169.9 (3)	O(4c)–Mo(5)–O(5d)	102.2 (3)	Mo(3)–O(3e)–Mo(8)	125.7 (3)	P–O(3f)–Mo(3)	125.5 (3)
O(2d)–Mo(5)–O(5e)	87.3 (2)	O(2f)–Mo(5)–O(5e)	73.0 (2)	P–O(3f)–Mo(7)	126.3 (3)	Mo(3)–O(3f)–Mo(7)	89.4 (2)
O(4c)–Mo(5)–O(5e)	155.3 (2)	O(5d)–Mo(5)–O(5e)	102.0 (3)	P–O(3f)–Mo(8)	125.7 (3)	Mo(3)–O(3f)–Mo(8)	89.1 (2)
O(2d)–Mo(5)–O(5f)	155.8 (2)	O(2f)–Mo(5)–O(5f)	85.3 (2)	Mo(7)–O(3f)–Mo(8)	89.1 (2)	Mo(4)–O(4c)–Mo(5)	151.3 (3)
O(4c)–Mo(5)–O(5f)	85.6 (2)	O(5d)–Mo(5)–O(5f)	103.8 (3)	Mo(4)–O(4d)–Mo(9)	126.7 (3)	Mo(4)–O(4f)–Mo(10)	150.9 (3)
O(5e)–Mo(5)–O(5f)	93.1 (2)	O(2e)–Mo(6)–O(2f)	72.7 (2)	Mo(5)–O(5e)–Mo(6)	126.2 (3)	Mo(5)–O(5f)–Mo(10)	151.0 (3)
O(2e)–Mo(6)–O(5e)	86.4 (2)	O(2f)–Mo(6)–O(5e)	71.6 (2)	Mo(9)–O(6c)–Mo(12)	151.4 (3)	Mo(6)–O(6f)–Mo(11)	151.0 (3)
O(2e)–Mo(6)–O(6e)	102.0 (3)	O(2f)–Mo(6)–O(6e)	169.2 (3)	Mo(7)–O(7e)–Mo(8)	125.5 (3)	Mo(7)–O(7f)–Mo(11)	152.1 (3)
O(5e)–Mo(6)–O(6e)	98.9 (3)	O(2e)–Mo(6)–O(6f)	155.3 (2)	Mo(8)–O(8c)–Mo(9)	152.0 (3)	Mo(8)–O(8f)–Mo(12)	150.1 (3)
O(2f)–Mo(6)–O(6f)	82.6 (2)	O(5e)–Mo(6)–O(6f)	84.4 (2)	Mo(6)–O(9f)–Mo(7)	150.7 (3)	P–O(10a)–Mo(10)	126.2 (3)
O(6e)–Mo(6)–O(6f)	102.0 (3)	O(2e)–Mo(6)–O(9f)	93.5 (2)	P–O(10a)–Mo(11)	125.4 (3)	Mo(10)–O(10a)–Mo(11)	88.7 (2)
O(2f)–Mo(6)–O(9f)	86.2 (2)	O(5e)–Mo(6)–O(9f)	156.8 (2)	P–O(10a)–Mo(12)	126.2 (3)	Mo(10)–O(10a)–Mo(12)	89.6 (2)
O(6e)–Mo(6)–O(9f)	103.7 (3)	O(6f)–Mo(6)–O(9f)	86.2 (2)	Mo(11)–O(10a)–Mo(12)	88.8 (2)	Mo(10)–O(10d)–Mo(12)	125.9 (3)
O(3d)–Mo(7)–O(3f)	71.7 (2)	O(3d)–Mo(7)–O(7d)	100.0 (3)	Mo(10)–O(10f)–Mo(11)	126.4 (3)	Mo(11)–O(11f)–Mo(12)	125.6 (3)
O(3f)–Mo(7)–O(7d)	170.4 (3)	O(3d)–Mo(7)–O(7e)	86.7 (2)	C(1a)–Na–C(3a)	126.8 (9)	C(1a)–Na–C(4a)	117.4 (9)
O(3f)–Mo(7)–O(7e)	73.5 (2)	O(7d)–Mo(7)–O(7e)	101.7 (3)	C(3a)–Na–C(4a)	115.8 (9)	Oa–C(1a)–Na	120.9 (9)
O(3d)–Mo(7)–O(7f)	155.3 (2)	O(3f)–Mo(7)–O(7f)	84.8 (2)	Oa–C(1a)–C(2a)	121.2 (9)	Na–C(1a)–C(2a)	117.9 (9)
O(7d)–Mo(7)–O(7f)	104.0 (3)	O(7e)–Mo(7)–O(7f)	93.9 (2)	C(1b)–Nb–C(3b)	124.9 (9)	C(1b)–Nb–C(4b)	119.4 (8)
O(3d)–Mo(7)–O(9f)	84.4 (2)	O(3f)–Mo(7)–O(9f)	82.6 (2)	C(3b)–Nb–C(4b)	115.7 (8)	Ob–C(1b)–Nb	120.3 (9)
O(7d)–Mo(7)–O(9f)	101.8 (3)	O(7e)–Mo(7)–O(9f)	156.0 (2)	Ob–C(1b)–C(2b)	120.9 (9)	Nb–C(1b)–C(2b)	118.8 (9)
O(7f)–Mo(7)–O(9f)	85.2 (2)	O(3e)–Mo(8)–O(3f)	73.1 (2)	C(1c)–Nc–C(3c)	126.7 (11)	C(1c)–Nc–C(4c)	117.3 (11)
O(3e)–Mo(8)–O(7e)	86.2 (2)	O(3f)–Mo(8)–O(7e)	71.8 (2)	C(3c)–Nc–C(4c)	116.0 (10)	Oc–C(1c)–Nc	122.1 (11)
O(3e)–Mo(8)–O(8c)	94.3 (2)	O(3f)–Mo(8)–O(8c)	85.6 (2)	Oc–C(1c)–C(2c)	119.9 (10)	Nc–C(1c)–C(2c)	118.0 (11)
O(7e)–Mo(8)–O(8c)	156.3 (2)	O(3e)–Mo(8)–O(8e)	101.6 (3)	C(1d)–Nd–C(3d)	126.4 (9)	C(1d)–Nd–C(4d)	118.6 (9)
O(3f)–Mo(8)–O(8e)	169.5 (2)	O(7e)–Mo(8)–O(8e)	99.0 (3)	C(3d)–Nd–C(4d)	115.0 (9)	Od–C(1d)–Nd	114.7 (9)
O(8c)–Mo(8)–O(8e)	104.0 (3)	O(3e)–Mo(8)–O(8f)	155.9 (2)	Od–C(1d)–C(2d)	118.5 (11)	Nd–C(1d)–C(2d)	126.6 (11)
O(3f)–Mo(8)–O(8f)	82.9 (2)	O(7e)–Mo(8)–O(8f)	84.8 (2)	C(1e)–Ne–C(3e)	126.0 (9)	C(1e)–Ne–C(4e)	118.3 (9)
O(8c)–Mo(8)–O(8f)	85.4 (2)	O(8e)–Mo(8)–O(8f)	101.8 (3)	C(3e)–Ne–C(4e)	115.7 (9)	Oe–C(1e)–Ne	119.2 (10)
O(1d)–Mo(9)–O(1f)	71.7 (2)	O(1d)–Mo(9)–O(4d)	86.7 (2)	Oe–C(1e)–C(2e)	120.8 (9)	Ne–C(1e)–C(2e)	119.9 (9)
O(1f)–Mo(9)–O(4d)	72.5 (2)	O(1d)–Mo(9)–O(6c)	155.9 (2)	C(1f)–Nf–C(3f)	128.9 (11)	C(1f)–Nf–C(4f)	115.2 (11)
O(1f)–Mo(9)–O(6c)	85.2 (2)	O(4d)–Mo(9)–O(6c)	93.0 (2)	C(3f)–Nf–C(4f)	116.0 (12)	Of–C(1f)–Nf	121.1 (10)
O(1d)–Mo(9)–O(8c)	85.4 (2)	O(1f)–Mo(9)–O(8c)	82.8 (2)	Of–C(1f)–C(2f)	119.8 (12)	Nf–C(1f)–C(2f)	119.2 (12)
O(4d)–Mo(9)–O(8c)	155.4 (2)	O(6c)–Mo(9)–O(8c)	85.0 (2)	C(1s)–C(2s)–Ns	176.4 (14)		

unexceptional for those of a heteropolymolybdate of the Keggin structure.[21,22a,23] The bond distances and angles in all six crystallographically unique DMA molecules, however, all show a higher degree of zwitterionic character than what would be predicted for an unassociated tertiary amide in accord with strong hydrogen bonding.

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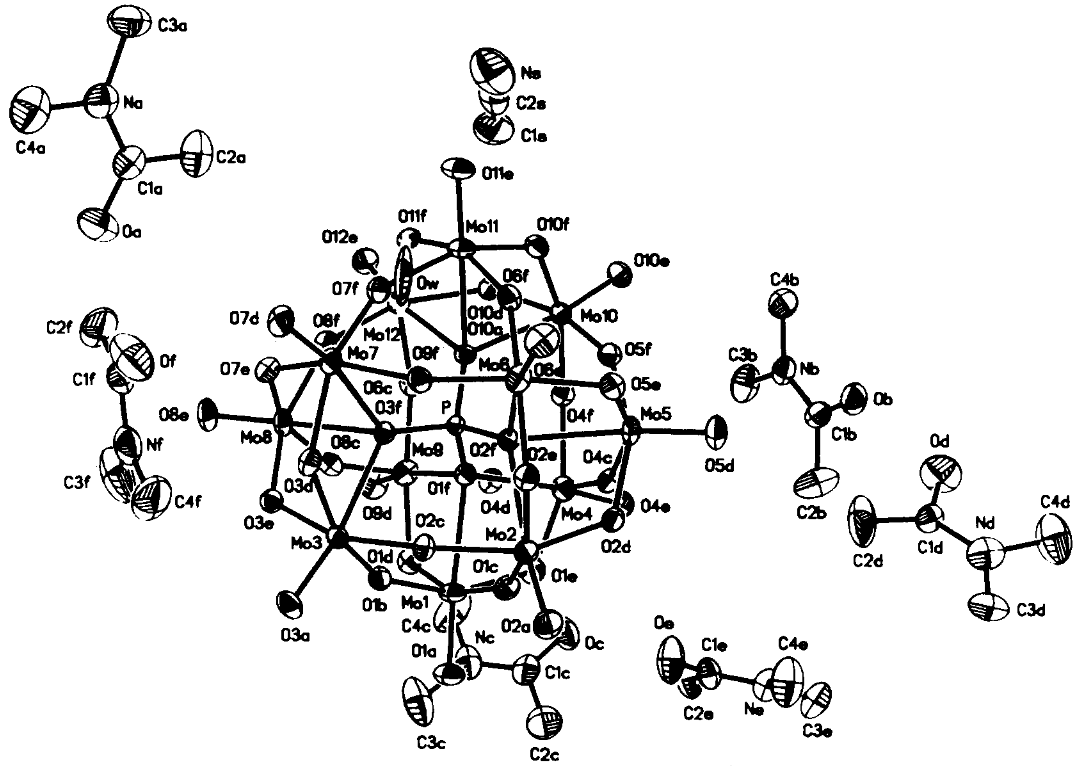

Figure 3. ORTEP and atom-numbering diagram for solvated **1**, α-$H_3PMo_{12}O_{40}$·6DMA·CH_3CN·$0.5H_2O$.[25] The hydrogen atoms are not indicated for clarity. Atoms are shown with 30% probability ellipsoids.

Table V. Short Solvate–Polyoxometalate Nonbonding Distances in **1**

solvate molecule	nearest nonbonded solvate non-H atom	α-$PMo_{12}O_{40}{}^{3-}$ O involved in bonding	dist, Å
	Shortest Contact for Each Solvate Molecule		
DMAb	C1b	O(5d)	2.994 (shortest)
DMAd	Od	O(12e)	3.024
DMAf	C1f	O(7d)	3.110
DMAa	C1a	O(6e)	3.119
DMAe	C4e	O(3d)	3.238
DMAc	C1c	O(11e)	3.299
CH_3CN	Ns	O(11e)	3.220
H_2O	Ow	O(6e)	3.331
	Other Short Contacts		
DMAb	Ob	O(5d)	3.038
DMAb	Ob	O(12e)	3.110
DMAa	Oa	O(1a)	3.180
DMAf	Of	O(7d)	3.152

A number of X-ray diffraction and neutron diffraction crystal structures have been carried out on conventional photochemically inactive heteropolyacids.[21-24] In most of these cases, the polyoxometalate protons are also involved in hydrogen bonding between the molecules of solvation, water molecules in the case of the literature studies. Examination of these literature structural investigations shows that the hydrogen-bonded water-containing counterions are nearly always more complex than discrete dimers as in the case of **1**.[24]

With the solvate–solvate interactions delineated, we now can turn to an analysis of the organic solvate–polyoxometalate interactions in **1**. Such an analysis should yield information addressing the effect of the DMA on the absorption and photochemical action spectra of the polyoxometalate. Table V summarizes the shortest distances between each of the eight organic solvate molecules (one acetonitrile, half of a water molecule, and six DMA molecules) and the polyoxometalate oxygens. The principal conclusion that follows from an examination of all the data on nonbonded distances for **1** including those data in Table V is that the interactions between the solvate molecules are generally far more substantial than the interactions between the solvate molecules and the polyoxometalate. The shortest DMA–polyoxometalate nonbonded distances are of two types; both involve the terminal oxo oxygens of the polyoxometalate (Table V). The first type of short nonbonded distance is to the DMA carbonyl carbons, and the second type is to the DMA carbonyl oxygens. These closest solvate–polyoxometalate distances are all quite long, in some cases barely shorter than the sum of the appropriate van der Waals radii. The lack of substantive structural interactions between the DMA moieties and the polyoxometalate moieties is unexpected and suggests that the origin of the effect of the DMA molecules on the electronic and photochemical action spectra of α-$PMo_{12}O_{40}{}^{3-}$ does not have a simple structural basis. The nature of the organic substrate–polyoxometalate electronic interactions in **1** is uncertain but may result from both secondary Coulombic and induced-dipole effects. The electronic transitions in complexes such as **1** could involve delocalized excited states or intermolecular donor–acceptor character. Studies currently in progress address these points.

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Registry No. 1·CH_3CN·$0.5H_2O$, 106455-70-3; DMA, 127-19-5; α-$H_3PMo_{12}O_{40}$, 12026-57-2.

Supplementary Material Available: Tables of thermal parameters, derived hydrogen positions, nonbonded distances, and torsion angles, a stereoview of the packing diagram (Figure S4) for α-$H_3PMo_{12}O_{40}$·6DMA·CH_3CN·$0.5H_2O$, and a plot of the DMAa-DMAf dimer interacting with adjacent polyoxometalate moieties (Figure S5) (22 pages); a listing of calculated and observed structure factors (54 pages). Ordering information is given on any current masthead page.

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