

required for a conformational rearrangement of the crown upon decomplexation. Table II shows that the large difference in  $\Delta H^\ddagger$  between acetone and methanol solutions on one hand and the acetone-dioxane mixture on the other is nearly exactly compensated by the change in  $\Delta S^\ddagger$ . Such a compensating effect is not uncommon when a given reaction is studied in a series of solvents;<sup>41</sup> for example, it was observed in the case of  $\text{Li}^+\cdot\text{C211}$  cryptates.<sup>33</sup>

In dioxolane the compensation is not quantitative although in this medium  $\Delta S^\ddagger$  is larger and  $\Delta G^\ddagger$  is larger by  $\sim 2$  kcal mol<sup>-1</sup> than in the other solvents.

We would like to suggest that the large  $\Delta H^\ddagger$  values in dioxolane as well as in a acetone-dioxane mixture is indicative of a weak solvation of the  $\text{K}^+$  ion in the transition state. In fact, Bhattacharyya et al.<sup>43</sup> have shown that the large alkali cations are almost not solvated by tetrahydrofuran. It would be expected that the same lack of solvation would be observed in 1,3-dioxolane.

(41) Laidler, K. J. "Chemical Kinetics"; McGraw-Hill: New York, 1965; p 251.

(42) Mei, E.; Popov, A. I.; Dye, J. L. *J. Am. Chem. Soc.* 1977, 99, 5308.

(43) Bhattacharyya, D. N.; Lee, C. L.; Smid, J.; Szwarc, M. *J. Phys. Chem.* 1965, 69, 608.

The mechanism I, which we found applicable in our systems, is also favored on stereochemical grounds. The 18C6 molecule is symmetrical, and the probabilities of an access of the cation to the 18C6 binding sites from both "faces" of the crown are identical. Likewise, in the  $\text{K}^+\cdot 18\text{C6}$  complex, in contrast to  $\text{Na}^+\cdot 18\text{C6}$ , the cation lies in the center of the crown ring.<sup>44</sup> The most likely transition state for mechanism I involves the symmetrical dicationic complex  $\text{K}^+\cdot 18\text{C6}\cdot\text{K}^+$ .

The slow exchange between free solvated alkali cation and its 18C6 complex presents many interesting aspects. Further studies are needed in other solvent systems before its nature can be clearly elucidated. Such studies are being continued in our laboratories.

**Acknowledgment.** We gratefully acknowledge the support of this work by the National Science Foundation Grant CHE-80-10808.

**Registry No.** K, 7740-09-2; 18C6, 17455-13-9; <sup>39</sup>K, 14092-91-2;  $\text{K}^+\cdot 18\text{C6}$ , 31270-13-0; THF, 109-99-9; 1,3-dioxolane, 646-06-0; acetone, 67-64-1; methanol, 67-56-1; 1,4-dioxane, 123-91-1.

(44) Wipff, G.; Weiner, P.; Kollman, P. *J. Am. Chem. Soc.* 1982, 104, 3249.

## Spectroscopic, Electrochemical, and Photochemical Properties of Molybdenum(II) and Tungsten(II) Halide Clusters

Andrew W. Maverick, Jan S. Najdzionek, Douglas MacKenzie, Daniel G. Nocera, and Harry B. Gray\*

Contribution No. 6533 from the Arthur Amos Noyes Laboratory, California Institute of Technology, Pasadena, California 91125. Received July 19, 1982

**Abstract:** The cluster ions  $\text{Mo}_6\text{Cl}_{14}^{2-}$ ,  $\text{Mo}_6\text{Br}_{14}^{2-}$ , and  $\text{W}_6\text{Cl}_{14}^{2-}$  are luminescent, with emission maxima (lifetimes, quantum yields) of 805 (180, 0.19), 825 (130, 0.23), and 880 nm (2  $\mu\text{s}$ , 0.02), respectively, in acetonitrile at room temperature. Absorption spectra at low temperature reveal weak shoulders at low energy ( $\text{Mo}_6\text{Cl}_{14}^{2-}$ , 530 and 590 nm;  $\text{Mo}_6\text{Br}_{14}^{2-}$ , 600 nm; and  $\text{W}_6\text{Cl}_{14}^{2-}$ , 490 and 550 nm) that may be electronically closely related to the luminescences. Solid  $(\text{Bu}_4\text{N})_2\text{Mo}_6\text{Cl}_{14}$  is rigorously diamagnetic, and the paramagnetic  $\text{Mo}_6\text{Cl}_{14}^-$  ion formed from it by one-electron oxidation gives an axial EPR spectrum ( $g_{\perp} = 2.10$ ;  $g_{\parallel} = 2.0$ ). All three ions undergo facile electrochemical oxidation, at potentials of 1.60, 1.38, and 1.14 V, respectively, vs. SCE in  $\text{CH}_3\text{CN}$ . Kinetics and rate constants are discussed for electron-transfer quenching of the luminescent excited state  $\text{Mo}_6\text{Cl}_{14}^{2-*}$  by several electron acceptors, both in aqueous and nonaqueous solutions, and for the subsequent electron-transfer reactions.

The halides of molybdenum(II) were first described by Blomstrand in 1859.<sup>1</sup> Soon afterwards the first report of the analogous tungsten compounds appeared.<sup>2</sup> Although various reports of the chemistry of these compounds suggested that they were polynuclear, the first definite structural characterization was a crystallographic study of  $[\text{Mo}_6\text{Cl}_8](\text{OH})_4\cdot 14\text{H}_2\text{O}$ .<sup>3</sup> The high overall symmetry of the staphylonuclear<sup>4</sup> cluster ion was established in 1950 by Vaughan in a crystal structure analysis of  $(\text{NH}_4)_2\text{Mo}_6\text{Cl}_{14}\cdot\text{H}_2\text{O}$ .<sup>5</sup> In idealized cubic symmetry, the  $\text{Mo}_6\text{Cl}_{14}^{2-}$  ion consists of an octahedron of metal atoms surrounded by eight face-bridging and six axial halides. The existence of the  $\text{M}_6\text{X}_8$  core has been demonstrated in a number of compounds: the dihalides  $\text{M}_6\text{X}_{12}$ , for example, are isomorphous, with the

central  $\text{M}_6\text{X}_8$  unit surrounded by four bridging and two terminal halides.<sup>6</sup>

Although substitution reactions are well documented for these cluster species, redox processes have previously been known to occur only with some difficulty and are often accompanied by major structural change. Our discovery that the clusters are intensely luminescent and undergo facile ground- and excited-state electron-transfer reactions<sup>7</sup> stimulated us to investigate more thoroughly the spectroscopic, electrochemical, and photochemical properties of  $\text{Mo}_6\text{Cl}_{14}^{2-}$ ,  $\text{Mo}_6\text{Br}_{14}^{2-}$ , and  $\text{W}_6\text{Cl}_{14}^{2-}$ . The data presented here shed new light on the electronic structure of the clusters.

### Experimental Section

**Cluster Compounds.** Molybdenum dichloride (Cerac, Inc.) was converted to  $(\text{H}_3\text{O})_2\text{Mo}_6\text{Cl}_{14}\cdot 6\text{H}_2\text{O}$  by the method of Sheldon.<sup>8</sup> This salt

(1) Blomstrand, W. *J. Prakt. Chem.* 1859, 77, 88-119. Molybdenum dichloride had probably been made before (see this paper; also Svanberg, L.; Struve, H. *Philos. Mag.* 1848, 33, 524-546 and references therein), but Blomstrand's work set the stage for its recognition as a cluster species.

(2) Roscoe, H. E. *Liebigs Ann. Chem.* 1872, 162, 349-368.

(3) Brosset, C. *Ark. Kemi, Mineral. Geol.* 1945, 20A, No. 7.

(4) Brosset, C. *Ark. Kemi, Mineral. Geol.* 1947, 25A, No. 19.

(5) Vaughan, P. A. *Proc. Natl. Acad. Sci. U.S.A.* 1950, 36, 461-464.

(6) Schäfer, H.; von Schnering, H.-G.; Tillack, J.; Kuhnen, F.; Wöhrle, H.; Baumann, H. *Z. Anorg. Allg. Chem.* 1967, 353, 281-310.

(7) Maverick, A. W.; Gray, H. B. *J. Am. Chem. Soc.* 1981, 103, 1298-1300.

(8) Sheldon, J. C. *J. Chem. Soc.* 1960, 1007-1014.

is readily soluble in acidic aqueous media and in many polar organic solvents. But it gradually loses water and HCl on standing, to some degree even in a closed container, to give a partially hydrolyzed product that is soluble only with difficulty. The potassium salt,<sup>9</sup> prepared by metathesis with KCl and recrystallized from 6 M HCl, was suitable for long-term storage without degradation. The ammonium salt,<sup>5</sup> also formed by metathesis, was used for measurements of spectra and extinction coefficients in aqueous solution.

Crude tungsten dichloride, as received from Varlacoid Chemical Co., was a black powder. Repeated extraction with hot 6 M HCl afforded bright lemon-yellow needles, slightly contaminated with small brown crystals. Finally the cluster was isolated as its ammonium salt, probably a hydrate, by metathesis with  $\text{NH}_4\text{Cl}$  in hot 6 M HCl, and dried over  $\text{P}_2\text{O}_5$  in a vacuum desiccator.

The tetrabutylammonium salts  $(\text{Bu}_4\text{N})_2\text{M}_6\text{X}_{14}$  were used for all experiments in nonaqueous solutions. The method of Sheldon<sup>10</sup> was adopted for  $(\text{Bu}_4\text{N})_2\text{Mo}_6\text{Br}_{14}$ , starting with molybdenum dibromide (Alfa) and substituting  $\text{Bu}_4\text{NBr}$  for  $\text{Et}_4\text{NBr}$ . For the molybdenum and tungsten chloride salts the method of Hogue and McCarley<sup>11</sup> sufficed, with  $\text{K}_2\text{Mo}_6\text{Cl}_{14}$  and  $(\text{NH}_4)_2\text{W}_6\text{Cl}_{14} \cdot x\text{H}_2\text{O}$ , respectively, as starting materials. The tetrabutylammonium salts, obtained originally as pale powdery precipitates from aqueous solution, were taken up in dichloromethane and the solutions dried over  $\text{Na}_2\text{SO}_4$ , filtered, and allowed to evaporate in air at room temperature. Prismatic crystals, some as large as 5-mm diameter, grew over a period of several days. Prominent faces of these crystals were hexagonal in outline and not noticeably dichroic, and showed parallel extinction and off-center biaxial optic axis interference figures between crossed polarizers. The crystals are probably monoclinic. Anal.  $(\text{C}_{32}\text{H}_{72}\text{N}_2\text{Mo}_6\text{Cl}_{14})$ ,  $(\text{C}_{32}\text{H}_{72}\text{N}_2\text{Mo}_6\text{Br}_{14})$ ,  $(\text{C}_{32}\text{H}_{72}\text{N}_2\text{W}_6\text{Cl}_{14})$  C, H, N.

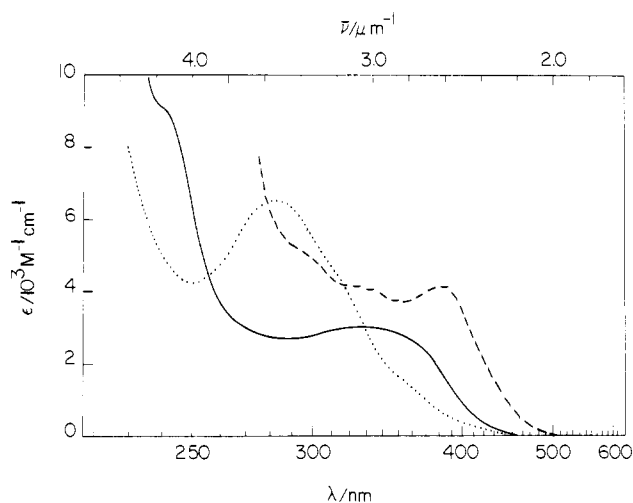
**Other Reagents.** Methylviologen (1,1'-dimethyl-4,4'-bipyridinium dichloride monohydrate) was purchased from Aldrich Chemical Co. and used without further purification.

A sample of BSEP (1,1'-bis(2-sulfoethyl)-4,4'-bipyridinium, inner salt) was obtained from G. McLendon. Additional quantities of BSEP and the homologue BSPP (1,1'-bis(3-sulfopropyl)-4,4'-bipyridinium, inner salt) were prepared by a modification of the method of Le Berre and co-workers.<sup>12</sup> Sulfoalkylation of 4,4'-bipyridine (dihydrate; Aldrich) was accomplished with 2-chloroethanesulfonyl chloride (Eastman) or 3-propane sulfone (3-hydroxypropanesulfonic acid, sultone; Aldrich)<sup>13</sup> in an acetic anhydride-acetic acid mixture (1:4 v/v). The crude products were precipitated from aqueous extracts of the reaction mixtures by flooding with ethanol, purified by treating with charcoal in aqueous solution and reprecipitating several times, and finally recrystallized from 0.1 M HCl, washed with ethanol, acetone, and dichloromethane, and air-dried. <sup>1</sup>H NMR for BSPP in  $\text{D}_2\text{O}$ :  $\delta$  2.3 (quintet, 4 H,  $\text{CH}_2$ ), 2.8 (t, 4 H,  $\text{CH}_2\text{SO}_3^-$ ), 4.7 (t, 4 H,  $\text{N}^+\text{-CH}_2$ ), 8.4, 9.0 (AB quartet, 8 H, aromatic). Chemical shifts estimated relative to DSS.

Samples of BSEP and BSPP isolated at intermediate stages by precipitation with ethanol tend to turn blue on standing. This suggests some kind of reductive decomposition. Bird and Kuhn<sup>14</sup> confirm that base hydrolysis of alkylviologens yields alcohols that can sometimes act as reductants, resulting in the spontaneous development of a blue color. Conducting the final crystallization in acidified water, however, appears to inhibit the decomposition and gives colorless crystals.

Extinction coefficients for BSEP<sup>•-</sup> and BSPP<sup>•-</sup> were measured in 0.1 mM solutions of the viologens in 0.08 M  $\text{NaHCO}_3$ -0.08 M  $\text{Na}_2\text{CO}_3$ , using excess  $\text{Na}_2\text{S}_2\text{O}_4$  as reductant. Spectra of these blue solutions were similar to that of  $\text{MV}^{\bullet+}$ , giving by comparison  $\epsilon_{595} = 8.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  for BSEP<sup>•-</sup> and  $\epsilon_{600} = 1.04 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for BSPP<sup>•-</sup>. Solutions 1 mM in these radical ions were violet, probably reflecting dimerization of the type observed by Kosower and Cotter with  $\text{MV}^{\bullet+}$ ,<sup>15</sup> but the low radical concentrations ( $<10^{-5}$  M) developed in flash photolysis make dimerization unfavorable.

Tetracyanoethylene (ethenetetracarboxynitrile, or TCNE; Aldrich) was recrystallized from chlorobenzene and vacuum sublimed. Chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) was obtained from MCB and



**Figure 1.** Electronic absorption spectra for the three cluster ions, as tetrabutylammonium salts in acetonitrile at room temperature: (—)  $\text{Mo}_6\text{Cl}_{14}^{2-}$ ; (---)  $\text{Mo}_6\text{Br}_{14}^{2-}$ ; (···)  $\text{W}_6\text{Cl}_{14}^{2-}$ .

recrystallized from toluene before use. Literature values<sup>16</sup> were used for extinction coefficients of the radical anions of these two quenchers.

Sodium 12-tungstophosphate,  $\text{Na}_3\text{PW}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$ , was prepared by the method of Wu,<sup>17</sup> stopping at the material he says "consists of sodium phospho-24-tungstate but is usually contaminated by traces of acid tungstates". This solid was recrystallized 3 times from 1 M  $\text{H}_2\text{SO}_4$  and once from 1 M HCl, collected, and air-dried. Potassium 12-tungstosilicate,  $\text{K}_4\text{SiW}_{12}\text{O}_{40} \cdot 18\text{H}_2\text{O}$ , was prepared following the procedure of Prados and Pope.<sup>18</sup>

Tetrabutylammonium trifluoromethanesulfonate,  $\text{Bu}_4\text{NTFMS}$ , was prepared following Brändström's general procedure,<sup>19</sup> using  $\text{Bu}_4\text{NH}_2\text{SO}_4$  (Aldrich) and redistilled  $\text{HTFMS} \cdot \text{H}_2\text{O}$  (from the anhydrous acid, 3M Co.). The product was crystallized by trituration with ether in an ice-salt bath, collected, and recrystallized from 2-propanol; yield ca. 80%.

Acetonitrile (UV) and dichloromethane were obtained from Burdick and Jackson Laboratories. For electrochemical studies the dichloromethane was used as received, and the acetonitrile was dried further by storage over activated alumina in a drybox. For spectroscopic and flash photolysis experiments these solvents were either distilled in vacuo from degassed, redistilled material stored over molecular sieves or used directly following degassing in five freeze-pump-thaw cycles. Hydrochloric acid (reagent) was diluted with an equal volume of water, treated with a small amount of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  to remove chlorine,<sup>20</sup> and distilled under argon. The constant-boiling distillate was diluted as required and used for flash photolysis after freeze-pump-thaw degassing.

**Instrumentation.** Absorption spectra were measured on Cary 17 and 219 spectrophotometers. Emission spectra were recorded on an apparatus built at Caltech (200 W Hg(Xe) lamp, Spex Minimate excitation monochromator and 436-nm bandpass filter, Spex 0.5-m emission monochromator, Hamamatsu R955 or cooled R406 photomultiplier, and PAR model 186A lock-in amplifier) and were corrected for monochromator and photomultiplier response. Dilute solutions, with absorbances less than 0.02 at 436 nm,<sup>21</sup> were used for quantum yield measurements and absolute quantum yields estimated by comparison with  $\text{Ru}(\text{bpy})_3^{2+}$ .<sup>22</sup> For low-temperature work, samples were mounted in a Cryogenics Technology Inc. Model 21 cryocooler.

Electrochemical measurements were made with PAR models 173, 175, and 179 electronics. For the cluster experiments, working and counter electrodes were platinum, the supporting electrolyte was 0.1 M

(9) Lindner, K.; Haller, E.; Helwig, H. *Z. Anorg. Allg. Chem.* **1923**, *130*, 209-228.

(10) Sheldon, J. C. *J. Chem. Soc.* **1962**, 410-415.

(11) Hogue, R. D.; McCarley, R. E. *Inorg. Chem.* **1970**, *9*, 1354-1360.

(12) Le Berre, A.; Étienne, A.; Dumaitre, B. *Bull. Soc. Chim. Fr.* **1970**, 954-958. The previously unreported BSPP has recently been described, but without synthetic details: Willner, I.; Otvos, J. W.; Calvin, M. *J. Am. Chem. Soc.* **1981**, *103*, 3203-3205.

(13) Sultones have been used before as sulfoalkylating agents: Helberger, J. H.; Manecke, G.; Heyden, R. *Liebigs Ann. Chem.* **1949**, *565*, 22-35.

(14) Bird, C. L.; Kuhn, A. T. *Chem. Soc. Rev.* **1981**, *10*, 49-82.

(15) Kosower, E. M.; Cotter, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 5524-5527.

(16) Webster, O. W.; Mahler, W.; Benson, R. E. *J. Am. Chem. Soc.* **1962**, *84*, 3678-3685. Foster, R.; Thomson, T. J. *Trans. Faraday Soc.* **1962**, *58*, 860-868. Extinction coefficients for TCNE<sup>•-</sup> and chloranil<sup>•-</sup> have been measured: Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7349-7350. For TCNE<sup>•-</sup> in  $\text{CH}_2\text{Cl}_2$ ,  $\epsilon_{469} = 4.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ; for chloranil<sup>•-</sup> in  $\text{CH}_3\text{CN}$ ,  $\epsilon_{483} = 2.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ .

(17) Wu, H. *J. Biol. Chem.* **1920**, *43*, 189-220.

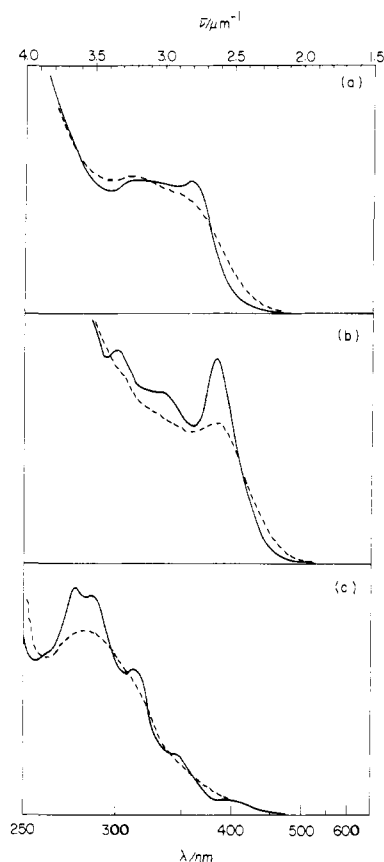
(18) Prados, R. A.; Pope, M. T. *Inorg. Chem.* **1976**, *15*, 2547-2553.

(19) Brändström, A.; Bernisson, P.; Carlsson, S.; Djurhuus, A.; Gustavii, K.; Junggren, U.; Lamm, B.; Samuelsson, B. *Acta Chem. Scand.* **1969**, *23*, 2202.

(20) Wilson, W. L. British Patent 739 144. See: *Chem. Abstr.* **1956**, *50*, 10 354a.

(21) Parker, C. A.; Rees, W. T. *Analyst (London)*, **1960**, *85*, 587-600.

(22) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853-4858.



**Figure 2.** Electronic absorption spectra in poly(methyl methacrylate) films: (---), room temperature; (—) ca. 30 K. (a)  $(\text{Bu}_4\text{N})_2\text{Mo}_6\text{Cl}_{14}$ ; (b)  $(\text{Bu}_4\text{N})_2\text{Mo}_6\text{Br}_{14}$ ; (c)  $(\text{Bu}_4\text{N})_2\text{W}_6\text{Cl}_{14}$ .

$\text{Bu}_4\text{NTFMS}$ , and the reference electrode was a silver-0.1 M  $\text{AgNO}_3$  (in  $\text{CH}_3\text{CN}$ ) couple. Cyclic voltammetry experiments performed on BSEP and BSPP utilized a hanging mercury drop working electrode and 1 M  $\text{CH}_3\text{SO}_3\text{H}$  supporting electrolyte.

EPR spectra were recorded on a Varian E-Line Century Series spectrometer equipped with an Air Products Heli-Tran cooling system. Magnetic susceptibility measurements were made at SHE Corp., San Diego, CA, with a SQUID-based Model 805 variable-temperature susceptometer with low-temperature option.

Stern-Volmer emission quenching experiments, using degassed solutions in standard 1-cm cells, were conducted on a Hitachi/Perkin-Elmer MPF-3 fluorescence spectrophotometer. Instruments built at Caltech were utilized for emission lifetime measurements (Nd:YAG laser (fwhm, 8 ns): 532-nm excitation) and microsecond flash photolysis experiments.<sup>23</sup> Unless otherwise noted, flash kinetic data were satisfactory over at least three half-lives of the absorbing species.

## Results and Discussion

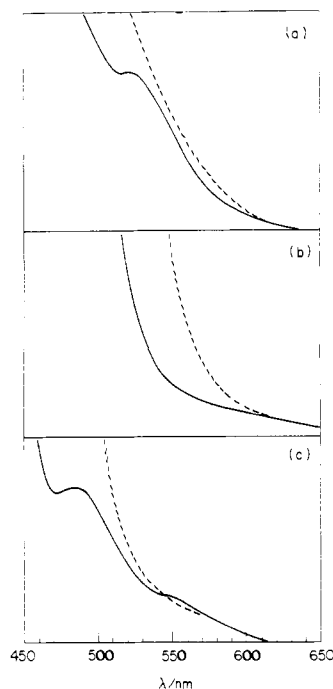
Solids and solutions containing the ions  $\text{Mo}_6\text{Cl}_{14}^{2-}$ ,  $\text{Mo}_6\text{Br}_{14}^{2-}$ , and  $\text{W}_6\text{Cl}_{14}^{2-}$  are yellow or orange in color. Their electronic absorption spectra, first recorded by Sheldon<sup>8,10,24</sup> in various aqueous solutions, are dominated by intense bands in the near-ultraviolet. These are illustrated in Figure 1 for tetrabutylammonium salts in acetonitrile at room temperature. Resolution in these spectra is perhaps somewhat superior to that of Sheldon, but to separate the broad absorptions into individual components has only been partially possible. Additional details are revealed at low temperature in poly(methyl methacrylate) films. Figure 2 allows comparisons of band intensity and position at ambient temperature and ca. 30 K.

The cluster ions are luminescent, both in solid state and in solution. Corrected emission spectral data are given in Table I. In contrast to the absorption spectra, whose major features are

**Table I.** Emission Spectroscopic and Electrochemical Data for  $(\text{Bu}_4\text{N})_2\text{M}_6\text{X}_{14}$

cluster ion	emission maxima/nm (fwhm/ $\mu\text{m}^{-1}$ )		$\tau/\mu\text{s}^a$	$\phi^a$	$E_{1/2}^b$ V vs. $\text{Ag}/\text{Ag}^+$ (vs. SCE)
	$\text{CH}_3\text{CN}$ solution: solid (300 K)	solid (30 K)			
$\text{Mo}_6\text{Cl}_{14}^{2-}$	805:805 (0.43)	830 (0.27)	180	0.19	1.29 (1.60)
$\text{Mo}_6\text{Br}_{14}^{2-}$	825:830 (0.43)	860 (0.26)	130	0.23	1.07 (1.38)
$\text{W}_6\text{Cl}_{14}^{2-}$	880:825 (0.37)	835 (0.25)	2	0.017	0.83 (1.14)

<sup>a</sup> Acetonitrile solution at 300 K; excitation wavelength 436 nm. Uncorrected value for  $\text{Mo}_6\text{Cl}_{14}^{2-}$  was 0.04 (ref 7). <sup>b</sup> Polarographic half-wave potentials ( $\text{M}_6\text{X}_{14}^{-/2-}$ ); acetonitrile solution at 300 K.



**Figure 3.** Absorption spectra (arbitrary units) for thick crystals: (---) room temperature; (—) ca. 30 K. (a)  $(\text{Bu}_4\text{N})_2\text{Mo}_6\text{Cl}_{14}$ ; (b)  $(\text{Bu}_4\text{N})_2\text{Mo}_6\text{Br}_{14}$ ; (c)  $(\text{Bu}_4\text{N})_2\text{W}_6\text{Cl}_{14}$ .

only slightly dependent on temperature, the emission spectra change substantially. At low temperature, the emission bands are much narrower in all three cases, and in the  $\text{Mo}_6\text{Cl}_{14}^{2-}$  and  $\text{Mo}_6\text{Br}_{14}^{2-}$  spectra there is a pronounced red shift. For all three clusters the overall emission intensity is substantially higher at low temperature.

The low-energy regions of the absorption spectra also display additional detail at low temperature. Figure 3 depicts absorption spectra for crystals of the ions' tetrabutylammonium salts, recorded at room temperature and at ca. 30 K. The room-temperature spectra are featureless, reflecting the gradual decrease in absorption associated with the intense bands in the near-ultraviolet. At low temperature, however, small shoulders can be seen. The new features appear at the following wavelengths (estimated  $\epsilon/\text{M}^{-1}\text{cm}^{-1}$  in parentheses):  $\text{Mo}_6\text{Cl}_{14}^{2-}$ , 530 (5) and 590 nm (0.5);  $\text{Mo}_6\text{Br}_{14}^{2-}$ , 600 nm (0.9); and  $\text{W}_6\text{Cl}_{14}^{2-}$ , 490 (0.6) and 550 nm (0.2). These absorption spectra offer limited resolution because the crystals fracture extensively on cooling; nevertheless, there are weak absorptions at relatively low energy in all three cluster ions in addition to the intense bands in the near-ultraviolet. It is likely that some of these low-energy transitions are associated directly with the ions' luminescent excited states. In agreement with this interpretation, luminescence is observed in solid

(23) Milder, S. J.; Goldbeck, R. A.; Klinger, D. S.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 6761-6764.

(24) Sheldon, J. C. *Nature (London)* **1959**, *184*, 1210-1213.

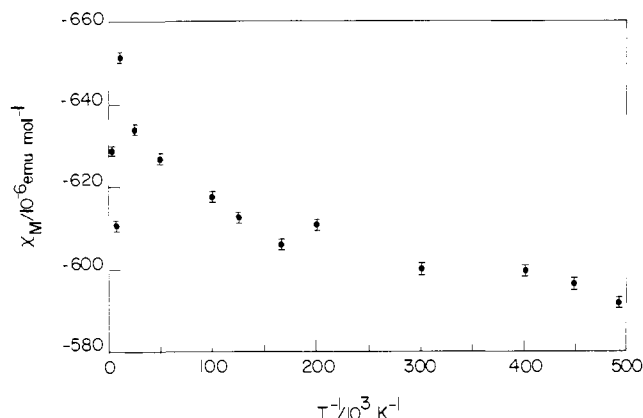


Figure 4. Magnetic susceptibility of powdered  $(\text{Bu}_4\text{N})_2\text{Mo}_6\text{Cl}_{14}$  as a function of reciprocal temperature. Raw data for this plot are available as supplementary material.

$(\text{Bu}_4\text{N})_2\text{Mo}_6\text{Cl}_{14}$  on excitation at 532 nm (Nd:YAG laser) even at ca. 30 K.

These data for weak absorption features can be compared with observed emission lifetimes (Table I), using the approximation of Strickler and Berg<sup>25</sup> for dipole-allowed transitions. For the weak shoulders at low energy in  $\text{Mo}_6\text{Cl}_{14}^{2-}$  (590 nm),  $\text{Mo}_6\text{Br}_{14}^{2-}$  (600 nm), and  $\text{W}_6\text{Cl}_{14}^{2-}$  (550 nm), the expected radiative lifetimes are 8, 3, and 24 ms, respectively, and the observed radiative lifetimes are 0.9, 0.6, and 0.1 ms, respectively (assuming unit quantum yield for formation of the excited state). At least for the Mo clusters the experimental results are in rough agreement with those predicted. In the case of  $\text{W}_6\text{Cl}_{14}^{2-}$ , the lack of accord with theory raises the possibility that the emission is attributable to an electronic transition that is more allowed than the one associated with the 550-nm absorption. Further studies on this and related tungsten clusters will be needed to resolve this issue. With the information in hand, however, we may conclude that the relatively long radiative cluster lifetimes are observable because nonradiative decay processes are so slow, probably due to the absence of high-energy vibrational modes for deactivation.

The diamagnetism of the clusters has rarely been questioned, the susceptibility of  $\text{Mo}_6\text{Cl}_{12}$  and most of its derivatives being negative at room temperature. However, standard diamagnetic corrections for the nonmetal atoms are generally greater than the measured diamagnetism. Briat and co-workers extended the susceptibility measurements on  $\text{Mo}_6\text{Cl}_{12}$  to low temperature, finding  $\chi_M = 3500 \times 10^{-6} \text{ emu mol}^{-1}$  at 4.2 K.<sup>26</sup> As additional evidence against a closed-shell ground state for the cluster they offered MCD spectra of  $\text{Mo}_6\text{Cl}_8^{4+}$ -containing poly(vinyl alcohol) films at 15 and 7.5 K, showing a number of signals whose intensity varied as  $T^{-1}$ . These MCD C terms exhibited extreme ellipticities at 380, 350, 310, 280, and 270 nm, in reasonable agreement with electronic absorption spectral data.

We were interested in studying the temperature dependence of the cluster's magnetic susceptibility, as the measurements at room temperature<sup>8</sup> and 4.2 K<sup>26</sup> appeared to conflict. Our data, however, show that the susceptibility remains negative even at 2 K (Figure 4),<sup>27</sup> thereby confirming that  $\text{Mo}_6\text{Cl}_{14}^{2-}$  has a closed-shell ( $^1A_{1g}$ ) ground state. On this point our work accords with several theoretical treatments<sup>28-31</sup> of the electronic structure of the clusters.

(25) Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814-822.

(26) Briat, B.; Rivoal, J. C.; Kahn, O.; Moreau, S. *Chem. Phys. Lett.* **1974**, *26*, 604-606. Briat, B.; Rivoal, J. C.; Kahn, O.; Moreau, S. *Proc. Int. Conf. Coord. Chem. 16th* **1974**, 2.25a.

(27) In view of the results of our magnetic measurements, the most likely explanation of the susceptibility and MCD data for  $\text{MoCl}_2$  in ref 26 is a small quantity of a paramagnetic impurity.

(28) Cotton, F. A.; Haas, T. E. *Inorg. Chem.* **1964**, *3*, 10-17.

(29) Guggenberger, L. J.; Sleight, A. W. *Inorg. Chem.* **1969**, *8*, 2041-2049.

(30) Gibson, J. F.; Meier, P. O. *W. J. Chem. Res., Synop.* **1978**, 66-67. *J. Chem. Res., Miniprint* **1978**, 946-956.

(31) Cotton, F. A.; Stanley, G. G. *Chem. Phys. Lett.* **1978**, *58*, 450-453.

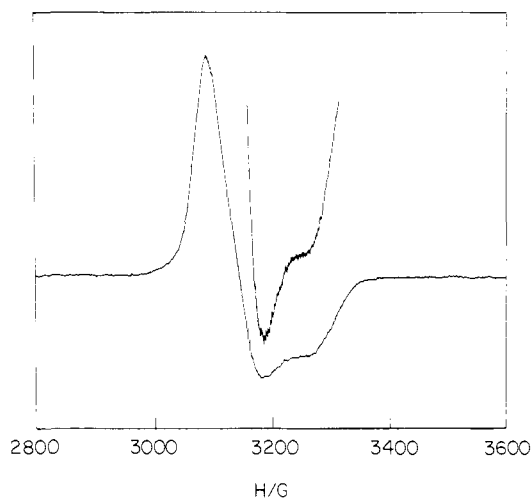


Figure 5. X-band (9.23 GHz) EPR spectrum recorded for electrochemically generated  $\text{Mo}_6\text{Cl}_{14}^-$  in frozen  $\text{CH}_2\text{Cl}_2$  (ca. 10 K).

Table II. Rate Constants for  $\text{Mo}_6\text{Cl}_{14}^{2-*}$  and  $\text{Mo}_6\text{Cl}_{14}^-$  Electron-Transfer Reactions

reactants	$k/\text{M}^{-1} \text{ s}^{-1}$ <sup>a</sup>	$E^\circ/\text{V}$ <sup>b</sup>
$\text{Mo}_6\text{Cl}_{14}^{2-*}/\text{TCNE} (\text{CH}_3\text{CN})$	$2.5 \times 10^9$	0.6 <sup>c</sup>
$\text{Mo}_6\text{Cl}_{14}^{2-*}/\text{BSEP} (2 \text{ M HCl})$	$3.8 \times 10^6$ <sup>d</sup>	~0
$\text{Mo}_6\text{Cl}_{14}^-/\text{TCNE}^- (\text{CH}_2\text{Cl}_2)$	$3.0 \times 10^9$ <sup>e</sup>	1.4
$\text{Mo}_6\text{Cl}_{14}^-/\text{chloranil}^- (\text{CH}_3\text{CN})$	$1.1 \times 10^8$ <sup>e</sup>	1.6 <sup>c</sup>
$\text{Mo}_6\text{Cl}_{14}^-/\text{BSEP}^- (2 \text{ M HCl})$	$1.0 \times 10^9$	~2

<sup>a</sup>  $\pm 20\%$ . <sup>b</sup> Driving force from electrochemical data. <sup>c</sup> Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Solutions"; Marcel Dekker: New York, 1970. <sup>d</sup> Based on lifetime from ref 7. <sup>e</sup> Based on extinction coefficients from ref 16.

The positions of the emission and weak absorption bands at low temperatures suggest excited-state energies of approximately 2.0 eV for all three cluster ions. As the energies of these bands are similar for  $\text{Mo}_6\text{Cl}_{14}^{2-}$  and  $\text{Mo}_6\text{Br}_{14}^{2-}$ , we believe that both HOMO and LUMO are largely metal centered. Additional information about the electronic structures of these clusters is contained in the EPR spectrum of a frozen solution of electrochemically generated  $\text{Mo}_6\text{Cl}_{14}^-$  (Figure 5). The signal can be accounted for by an axially symmetric  $S = 1/2$  system,  $g_\perp = 2.10$  and  $g_\parallel = 2.0$ . It is apparent from the symmetry of this spectrum that  $\text{Mo}_6\text{Cl}_{14}^-$  is axially distorted in some way.<sup>32</sup> Although there are several possible explanations for the apparent reorganization, an attractive one consistent with the values of the  $g$  tensor components is that an  $e_g$  cluster orbital is depopulated on oxidation, and that as a result the parent  $O_h$  cluster undergoes a tetragonal distortion to give a  $^2A_{1g}(D_{4h})$  or  $^2A_1(C_{4v})$  ground state for  $\text{Mo}_6\text{Cl}_{14}^-$ . Determination of the nature of the Mo-Mo and Mo-Cl interactions in the half-occupied cluster orbital will require a full analysis of the  $g$  parameters based on structural information for the oxidized ion that is not available at present.

All three cluster ions undergo simple one-electron oxidation in aprotic solvents (Table I gives half-wave potentials extracted from cyclic voltammograms for the ions in  $\text{CH}_3\text{CN}$ ).<sup>33,34</sup> The  $\text{M}_6\text{X}_{14}^-$  ions are powerful oxidizing agents, rivaled by only a few

(32) Gibson and Meier also attributed an axial EPR signal in  $\gamma$ -irradiated  $\text{Mo}_6\text{Cl}_{12}$  to a species formed by one-electron oxidation of the  $\text{Mo}_6\text{Cl}_8^{4+}$  core.<sup>30</sup> However, their spectra are of poor quality and the  $g$  values extracted are inconsistent with those reported here.

(33) Cathodic waves were observed for all three ions and additional anodic waves for  $\text{Mo}_6\text{Br}_{14}^{2-}$  and  $\text{W}_6\text{Cl}_{14}^{2-}$ , but these were more complicated and not easily resolved.

(34) Plots of peak anodic current vs. (scan rate)<sup>1/2</sup> were linear over the following ranges:  $\text{Mo}_6\text{Cl}_{14}^{2-}$ , 20  $\text{mV s}^{-1}$  to 500  $\text{V s}^{-1}$ ;  $\text{Mo}_6\text{Br}_{14}^{2-}$ , 20  $\text{mV s}^{-1}$  to 1  $\text{V s}^{-1}$ ;  $\text{W}_6\text{Cl}_{14}^{2-}$ , 50-350  $\text{mV s}^{-1}$ . The ratio of cathodic and anodic peak currents, calculated by using Nicholson's approximation (Nicholson, R. S. *Anal. Chem.* **1966**, *38*, 1406), approaches unity at high scan rates for all three ions. At lower scan rates, however, the ratio drops significantly, showing that the oxidized ions are unstable over long periods of time.

chemical oxidants. Also, the positions of the oxidation waves relative to those of  $X^-$  ions confirm that the halides in  $M_6X_{14}^{2-}$  are firmly bound.

Bulk electrolysis experiments were also performed in order to prepare the oxidized  $M_6X_{14}^-$  species in pure form. An initial attempt to prepare  $Mo_6Cl_{14}^-$  in  $CH_3CN$  failed. In dichloromethane, however, oxidations of  $Mo_6Cl_{14}^{2-}$  and  $W_6Cl_{14}^{2-}$  were quantitative. In both cases cyclic voltammograms were unchanged during electrolysis. Absorption spectra of the electrolyzed  $Mo_6Cl_{14}^{2-}$  and  $W_6Cl_{14}^{2-}$  solutions show new bands at 480 and 420 nm, respectively. Although oxidation of  $Mo_6Br_{14}^{2-}$  is also quantitative under these conditions, new peaks appear in the cyclic voltammogram during electrolysis, indicating that following reactions are occurring.

Rate constants obtained for photochemical electron-transfer reactions in the  $Mo_6Cl_{14}^{2-}$  system are summarized in Table II. Our initial studies of oxidative quenching by  $MV^{2+}$  have been described previously.<sup>7</sup> Further use of  $MV^{2+}$  in this system was complicated by a solubility problem: it forms a precipitate with  $Mo_6Cl_{14}^{2-}$  which is nearly insoluble in aqueous HCl and only sparingly soluble in  $CH_3CN$ . Other experiments were performed with neutral and anionic quenchers to circumvent this problem. The criterion used to determine reversible electron-transfer chemistry in these experiments was the successful fitting of data for the back-electron-transfer reaction to the expected second-order kinetics. Flash kinetic spectroscopic experiments in aqueous solution were restricted to 2–3 M HCl. It appeared that, if the use of  $MV^{2+}$  as quencher was hampered by a solubility problem, sulfonation might solve that problem by making the viologen a zwitterion. Thus, the best results in aqueous solution were obtained with the sulfoalkylated bipyridines BSEP and BSPP (in the case of BSEP, the kinetics of the back-electron-transfer reaction were satisfactory over a range of at least a factor of 4 in [BSEP]).

As a set of quenchers for aqueous solutions, the Keggin  $XW_{12}O_{40}$  heteropolytungstates appeared ideal for several reasons. First, especially in the presence of heterogeneous catalysts, the viologens are subject to hydrogenation,<sup>14</sup> which wastes stored energy and destroys their electron-relay properties. Second, the heteropoly ions undergo clean electron-transfer reactions in acidic aqueous solutions. Here the choice of central atom X (for example, from the series  $PW_{12}O_{40}^{3-/4-}$ ,  $SiW_{12}O_{40}^{4-/5-}$ , and  $BW_{12}O_{40}^{5-/6-}$ ) in the Keggin ions allows variation both in charge and in redox potential (–0.07, –0.27, –0.58 V vs. SCE, respectively).<sup>18</sup> Thus, under conditions (2–3 M HCl) employed in these studies, both  $SiW_{12}O_{40}^{5-}$  and  $BW_{12}O_{40}^{6-}$  are thermodynamically capable of reducing  $H^+$  to  $H_2$ . And finally, the fully oxidized W(VI) species are colorless, while the one-electron reduced “heteropoly blues” show broad absorption in the red and near-infrared region.<sup>35</sup> Unfortunately, although the heteropoly ions appear to quench the

$Mo_6Cl_{14}^{2-}$  luminescence efficiently (see below), repeated trials in flash kinetic spectroscopic experiments failed to confirm second-order behavior for the back-electron-transfer reaction.

Quenching rate constants also given in Table II were determined by Stern–Volmer analysis of emission quenching data. Preliminary data, also in 2 M HCl, for BSPP,  $SiW_{12}O_{40}^{4-}$ , and  $PW_{12}O_{40}^{3-}$  suggest rate constants of approximately  $3 \times 10^6$ ,  $2 \times 10^8$ , and  $7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. The quenching rate constants of Table II, and the above preliminary data, display the expected parallel trends of rate constant and thermodynamic driving force.

Combining the results of the electrochemical and photophysical investigations, we have been able to show that the luminescent excited state of  $Mo_6Cl_{14}^{2-}$  is capable of rapid reaction with electron acceptors. The powerfully oxidizing  $Mo_6Cl_{14}^-$  is produced in these reactions. The data for BSEP in particular confirm that the ion's attractive photochemical properties, originally inferred from its photophysical and electrochemical behavior in nonaqueous media, are retained in aqueous solution as well. These properties, namely the presence of long-lived excited states and the capacity for rapid thermal and photochemical redox reactions without major structural change, are expected to persist in the  $Mo_6Br_{14}^{2-}$  and  $W_6Cl_{14}^{2-}$  ions also.

Thus, these clusters represent a new class of photoreceptors for light-induced chemical reactions. They are chemically stable under a variety of conditions, and they undergo facile electron-transfer reactions in their ground and excited states. We are continuing our studies of spectroscopic and photoredox properties of these ions and their derivatives. Also, on the basis of the established properties of the  $W_6Br_8^{4+/6+}$  system<sup>36,37</sup> and on the observation of additional oxidation and reduction processes in electrochemical experiments, we are investigating the possibility of photochemical multielectron-transfer reactions using these ions.

**Acknowledgment.** We thank G. McLendon for a sample of BSEP. This research was supported by National Science Foundation Grant CHE81-20418. Startup funds were provided by a DOE energy research program grant to Caltech (DE-FG03-76ER10058). A.W.M. acknowledges the National Science Foundation (1977-1980) and the Standard Oil Co. (Ohio) (1980-1981) for graduate fellowships; D.G.N. thanks the Sun Company (1982) for a graduate fellowship.

**Registry No.**  $Mo_6Cl_{14}^{2-}$ , 51364-21-7;  $Mo_6Br_{14}^{2-}$ , 52906-24-8;  $W_6Cl_{14}^{2-}$ , 47021-01-2;  $Mo_6Cl_{14}^-$ , 84680-78-4;  $(Bu_4N)_2Mo_6Cl_{14}$ , 12367-12-3;  $(Bu_4N)_2Mo_6Br_{14}$ , 84648-01-1;  $(Bu_4N)_2W_6Cl_{14}$ , 84648-02-2.

**Supplementary Material Available:** Magnetic susceptibility data for  $(Bu_4N)_2Mo_6Cl_{14}$  (1 page). Ordering information is given on any current masthead page.

(36) Schäfer, H.; Siepmann, R. *Z. Anorg. Allg. Chem.* **1968**, 357, 273–288.

(37) Siepmann, R.; von Schnering, H.-G. *Z. Anorg. Allg. Chem.* **1968**, 357, 289–298.

(35) Varga, G. M., Jr.; Papaconstantinou, E.; Pope, M. T. *Inorg. Chem.* **1970**, 9, 662–667.