Table II. Assignments of Measured Ligand Field Bands (in cm^{-1}) for K_3NbF_7 in Slightly Distorted D_{5h} Symmetry[a]

Measd freq		D_{5h} assignment
28,570		$a_1'(z^2)$
19,762 16,556	$\Delta = 3206$	$e_2'[(x^2 - y^2), (xy)]$
2150 0	$\Delta = 2150$	$e_1''[(yz), (zx)]$

[a] Splitting denoted by Δ.

quencies causing the appearance of its shoulder at 4000 cm^{-1} in Figure 2. Attempts to demonstrate the temperature shift of this band failed because of instrument limitations. Nevertheless its appearance at 2150 cm^{-1} is consistent with what would be predicted on comparison with the splitting observed for the e_1' state. Table II summarizes the assignments which have been made for the electronic spectra.

The spectrum of K_3NbF_7 can be related to previously reported spectra of D_{5h} complexes involving V(III)[10] and Ti(III).[11] Using the notation of Levenson and Dominguez,[10] $10\delta_1$ and $10\delta_1 + 10\delta_2$ for NbF_7^{3-} are found to be 17,084 and 28,570 cm^{-1}, respectively, from average values for the e_1'' and e_2' states shown in Table II. These values for Nb(IV) (when compared with those in Table III of ref 10) are equivalent to those measured for V(III) and considerably greater than those measured for Ti(III). In spite of the lower position of F^- relative to CN^- in the spectrochemical series, the second-row transition elements especially with a greater charge would be expected to compensate for the effect of the weaker ligand. Thus the energies measured for d-d electronic transitions in NbF_7^{3-} are not viewed as unusual.

In conclusion, these assignments represent the complete ligand field spectrum of a seven-coordinated Nb(IV) ion in a field of slightly distorted D_{5h} symmetry. The effect of higher temperatures causes further distortion of the D_{5h} field as shown by the increase in the splitting of the originally degenerate states. In the limit, all four electronic bands should appear in the 4000–40,000-cm^{-1} region. Such a spectrum would be anticipated for a seven-coordinated Nb(IV) ion in a solution containing a random arrangement of ligands about the cations.

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Registry No. KF, 7789-23-3; NbF_5, 7783-68-8; Nb, 7440-03-1; K_3NbF_7, 51773-97-8.

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(11) M. G. B. Drew, G. W. A. Fowles, and D. F. Lewis, *Chem. Commun.*, 876 (1969).

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New Molybdenum(II) and Molybdenum(III) Species

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The preparations of $Mo(H_2O)_6{}^{3+}$, of a species with NH_3 coordinated to Mo(III) which we take to be $[Mo(NH_3)_4(H_2O)HCO_2]^{2+}$, of $K_4Mo_2(SO_4)_4$, of $Mo_2(en)_4Cl_4$, of $Mo_2{}^{4+}(aq)$, and of miscellaneous related compounds are described. The continued investigation of $Mo(H_2O)_6{}^{3+}$ and of $Mo_2{}^{4+}(aq)$ has led to a revision of the absorption spectra reported earlier. For $Mo(H_2O)_6{}^{3+}$, in place of the strong peaks in the uv region reported earlier, which we now believe were caused by Mo(V) present in trace amounts, we find λ_{max} at 308 nm (ϵ 28 ± 1.4 $M^{-1}\ cm^{-1}$) and at 370 nm (ϵ 16 ± 0.8 $M^{-1}\ cm^{-1}$) and attribute these bands to spin-allowed d–d transitions. For $Mo_2{}^{4+}(aq)$ we find λ_{max} at 504 nm (ϵ 337 $M^{-1}\ cm^{-1}$) and at 370 nm (ϵ 40 $M^{-1}\ cm^{-1}$). For $Mo_2(en)_4{}^{4+}$, three bands are observed: 478 nm (ϵ 483), 360 nm (ϵ 36), and 235 nm (ϵ 966). Qualitative observations on some reactions of $Mo(H_2O)_6{}^{3+}$, $Mo_2(en)_4{}^{4+}$, and $Mo_2{}^{4+}(aq)$ are reported.

As part of a program of research devoted to extending the chemistry of complexes of second and third row transition elements in low oxidation states, in combinations stressing saturated ligands, we have attempted to prepare aquo ions of Mo(III) and Mo(II) and of ammine or related complexes as well.

Hartmann and Schmidt[1] reported ligand field spectra of Mo(III) species prepared in 4 *M* hydrochloric, hydrobromic, or sulfuric acid, and from the fact that the spectra were found to be rather insensitive to the nature of the anion, they concluded that the green species they had in hand was the same in the different media and that it therefore was $Mo(H_2O)_6{}^{3+}$. This claim was disputed by Bowen and Taube[2] who outlined an alternative method for preparing what they believed to be $Mo(H_2O)_6{}^{3+}$, describing the species as being virtually colorless. Their conclusions as stated were supported by Kustin and Toppen,[3] who did, however, point out that the uv bands reported by Bowen and Taube[2] are not properties of $Mo(H_2O)_6{}^{3+}$.

In this paper, details of the preparation and characterizations of $Mo(H_2O)_6{}^{3+}$ are reported. We concede the correction to our earlier work on the matter of the uv spectrum of $Mo(H_2O)_6{}^{3+}$ and report values for the intrinsic spectrum more nearly in accord with expectations for absorption arising from d–d transitions. Work on the preparation of species containing NH_3 in the first coordination sphere of Mo(III) is also described. Little has been reported on the chemistry of the important class of saturated ligand complexes, namely the ammines. Rosenheim, *et al.*,[4] have claimed to have prepared the complexes $[MoCl_3(NH_3)_3]$, $[MoCl_2(NH_3)_4]Cl$, and [Mo-

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(1) H. Hartmann and H. J. Schmidt, *Z. Phys. Chem. (Frankfurt am Main)*, **11**, 134 (1957).

(2) A. R. Bowen and H. Taube, *J. Amer. Chem. Soc.*, **93**, 3287 (1971).

(3) K. Kustin and D. Toppen, *Inorg. Chem.*, **11**, 2851 (1972).

(4) A. Rosenheim, G. Abel, and R. Levy, *Z. Anorg. Allg. Chem.*, **197**, 189 (1931).

$(NH_3)_6]Cl_3$. However, in the light of later work,[5] their conclusions on the nature of the material they had on hand seem to be incorrect.

In contrast to chromium(II), no monomeric compounds of molybdenum(II) with saturated ligands are known. Molybdenum(II) complexes are usually stabilized by metal to metal bonds or by unsaturated ligands. Of particular moment for us was the work by Brencic and Cotton[6] on compounds such as tetrapotassium octachlorodimolybdate(II). In the ion $Mo_2Cl_8{}^{4-}$ the molybdenum–molybdenum bond distance is 2.16 Å, and Brencic and Cotton postulated a quadruple bond between the molybdenum atoms.

As before,[2] the octachlorodimolybdate anion was the starting material in the preparation of the aquodimolybdate(II) cation, but the preparation has since been refined. It was the starting material, also, for the preparation of the other complexes of Mo(II) which are dealt with in this paper.

Experimental Section

Reagents. Molybdenum hexacarbonyl was donated by the Climax Molybdenum Co. Potassium hexachloromolybdate(III) was used as obtained from Alfa Inorganics. It was stored under argon when not in use. The Dowex 50W-X2 resin from Bio-Rad was cleaned as described by Deutsch[7] and stored dry in the dark. The strongly acidic cationic Sephadex resin, SP-Sephadex C-50, obtained from Pharmaceia was used without further purification. The argon was bubbled through two chromous solution–zinc amalgam reductors in series to remove oxygen. The water was doubly distilled, the second distillation being made from an alkaline potassium permanganate solution. All other chemicals were reagent grade and were used without purification.

The trifluoromethylsulfonic acid, HSO_3CF_3, was obtained from Minnesota, Mining, and Manufacturing Co. and distilled under slightly reduced pressure before use.

Instruments and Techniques. Visible and ultraviolet absorption spectra were taken on a Cary Model 14 or a Cary Model 15 recording instrument, and ir spectra on a Perkin-Elmer instrument, Model 237 B. Magnetic susceptibility studies on solids were carried out on a Faraday Magnetic Susceptibility System from Cahn instruments.

All the aqueous solutions involving molybdenum were deaerated with argon for at least 1 hr so as to remove oxygen from the solutions. All manipulations with molybdenum(II) and -(III) compounds were done under argon.

The ion-exchange separations involving molybdenum were done under argon at 5°. In order to purge the entire ion-exchange apparatus and the resin with argon, 200 ml of deareated water was transferred to the column and the resin was purged by passing argon through the supporting glass frit for 30 min. Then the resin was allowed to settle and the water to pass through, after which the column was treated with 50 ml of 0.25 *M* solution of chromous ion, in 1.0 *M* hydrochloric acid. The chromous ion was eluted from the column with 300 ml of 3 *M* hydrochloric acid. Following this, deaerated water was passed through the resin until the eluate gave no precipitate with silver ion. This procedure was usually carried out on 20–30 ml of wet Ag 50W-X2 resin before ion-exchange experiments with molybdenum species were attempted. When a Sephadex resin was used, sodium tosylate or sodium trifluoromethylsulfonate replaced hydrochloric acid.

The mean oxidation state of molybdenum was determined by relying on the Stanford Microanalytical Laboratory for molybdenum analysis and determining the reducing capacity as follows. At least a tenfold excess of 0.2 *M* ferric solution in 1 *M* sulfuric acid was added to the Mo-containing solution. The solution was then titrated with a ceric solution which was 2 *M* in sulfuric acid using ferroin as indicator. The formate,[8] the sulfate,[9] and the ammonia analyses[10] are described elsewhere.

The syntheses of tetrapotassium octachloromolybdate[6] and of tripotassium hexacarbonyl-μ-triol-dimolybdate(0)[11] followed the literature procedures.

Results and Discussion

A. Preparation and Characterization of Mo(III) Species. Mo^{3+}(aq). The method of preparation of $Mo(H_2O)_6{}^{3+}$ depends on the aquation of $MoCl_6{}^{3+}$ ion in a solution containing a strong acid, the anion of which is noncomplexing and does not oxidize Mo(III). Trifluoromethylsulfonic acid appears to meet both requirements and was used in most of the studies.[12]

In a typical preparation, 1 g of K_3MoCl_6 was dissolved in 50 ml of 2 *M* HSO_3CF_3 with argon as a blanketing gas, the solution being kept shielded from light. The solution was initially bright red, after 3 hr orange, after 1.5 days yellow, and after 4 days a faint greenish yellow.

The ion-exchange work was done at 5° with 30 ml of Ag 50-X2 resin in a three-stage column, one stage 5 mm in diameter and 5 cm in length, the next 7 mm and 5 cm, and the last 9 mm and 5 cm. The solution was diluted to 250 ml before being placed on the column. While the column was being charged, a thin red band developed at the top and a greenish solution passed through. The red species could be eluted with 4 *M* HSO_3CF_3 and had an oxidation state averaging 4.4 ± 0.1. This material probably contained a species described in a recent article by Ardon, *et al.*[13] In order to remove any dipositive species, 200 ml of 0.5 *M* HSO_3CF_3 was passed through the column. Then 1.0–1.5 *M* HSO_3CF_3 was used to elute the hexaaquomolybdenum(III) cation.

The mean oxidation state, based on number of runs, of the molybdenum eluted from the column as $Mo(H_2O)_6{}^{3+}$ was found to be 3.05 ± 0.15. The chloride content of the solution was found to be less than 2% of that of the molybdenum on a molar basis. Experiments to determine the ionic charge for molybdenum, using the ion-exchange technique failed, there being decomposition on the column whenever a salt solution at low acidity was used as eluent. The mobility of the species on the column, however, is consistent with a charge of 3+.

In the light of work done by others[3,14] on $Mo(H_2O)_6{}^{3+}$ subsequent to ours, we undertook a reinvestigation of the absorption spectrum of the ion, but using improved procedures for the cation-exchange work. (The chief improvement introduced was probably that of adding a step in which the resin in the column was treated with Cr^{2+}(aq) to reduce oxidizing impurities.)

A typical spectrum for $Mo(H_2O)_6{}^{3+}$ prepared by the improved route covering the near-uv region is shown in Figure 1. Band maxima are observed at 308 mm (ϵ 28 ± 1.4) and at 370 mm (ϵ 16 ± 0.8). The positions of these bands seem reasonable in comparison[15] to those observed for $Mo(urea)_6{}^{3+}$[16] in the solid, at 322 and 386 nm, respectively, and their intensity seems in accord with assignment to the $^4T_{1g}(F) \leftarrow {}^4A_{2g}$ and $^4T_{2g} \leftarrow {}^4A_{2g}$ transitions, respectively. These assignments would fix 10*Dq* for $Mo(H_2O)_6{}^{3+}$ as 27,000 cm^{-1} compared to 17,400 cm^{-1} for $Cr(H_2O)_6{}^{3+}$.

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(8) A. I. Vogel, "A Text-book of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis," 3rd ed, Wiley, New York, N. Y., 1966.

(9) D. A. Skoog and D. M. West, "Fundamentals of Analytical Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1963.

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(14) M. Ardon, private communication.

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(16) T. Komorita, S. Miki, and S. Yamada, *Bull. Chem. Soc. Jap.*, **38**, 123 (1965).

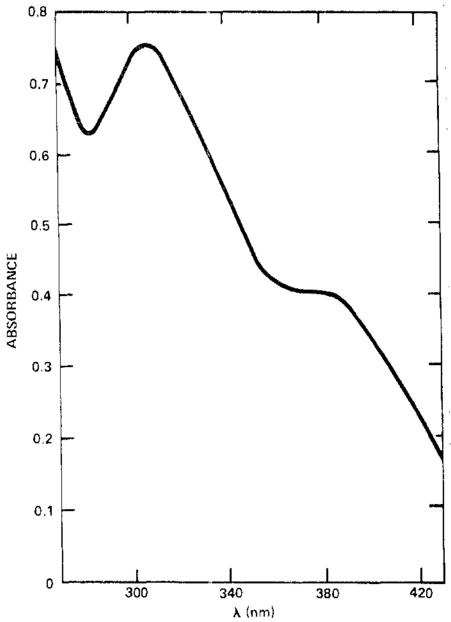

Figure 1. Absorption spectrum of $Mo(H_2O)_6{}^{3+}$. [Mo(III)] = 5.7 × 10^{-3} *M*; $[HSO_3CF_3]$ = 1.0 *M*; 5-cm cell.

In one preparation with a solution 0.004 *M* in $Mo(H_2O)_6{}^{3+}$ in a 5-cm cell a very weak band ($\epsilon < 1$) was observed at 635 mm. This may be the spin-forbidden transition.

Our spectrum for $Mo(H_2O)_6{}^{3+}$ in the near-uv region is in reasonably good agreement with that recently published by Sasaki and Sykes.[17] In view of the ease of oxidation of $Mo(H_2O)_6{}^{3+}$ and the sensitivity of the spectrum to the products of oxidation, it is useful to have independent measurements of this important property.

The magnetic moment of a solution *ca.* 1 *M* in HSO_3CF_3 with Mo(III) at 0.006 *M* was determined by the Evans method.[18] The effective magnetic moment calculated from a determination at a single temperature, 25°, was found to be 3.6 BM. This value is in reasonable agreement with that of 3.7 BM determined by Kustin and Toppen.[3]

Reaction of $Mo(H_2O)_6{}^{3+}$ with O_2. When a solution containing $Mo(H_2O)_6{}^{3+}$ is exposed to O_2, a band appears at 292 nm, after *ca.* 20 min reaches a maximum in intensity, and then decrease in intensity over a period of hours. The species present in solution when the intensity of the band at 292 nm reaches a maximum is found to have a mean oxidation number for Mo of 5. As judged by its elution behavior on a catonic exchange resin, the species appears to have a charge of 2+. In view of other work on Mo(V) in acidic HCl or HBr and recent work[19] in the presence of noncomplexing anions, it is reasonable to suppose that the species we are dealing with is dimeric. On reduction of the Mo(V) species with amalgamated zinc, a green product is formed having a spectrum similar to that described by Hartmann and Schmidt.[1]

Ammine Complexes of Mo(III). When K_3MoCl_6, which is a red solid, was kept at 25° under liquid NH_3 containing NH_4Cl for 3 weeks and the liquid was then decanted, a brown-orange solid was left. The solid was washed with cold water (it appears to be insoluble in water) and ethanol and dried. *Anal.* Calcd for $Mo(NH_3)_3Cl_3$: Mo, 37.9; N, 16.6; Cl, 40.8. Found: Mo, 34.0; N, 15.5; Cl, 37.6. The mean oxidation number of Mo in the solid was determined as 3.0 ± 0.2.

It is likely that the solid prepared as described above is largely composed of $Mo(NH_3)_3Cl_3$, but the material did not prove to be useful for the preparation of ammine complexes in solution. An alternative method which will now be described does appear to be a route, though not an efficient one, to the preparation of complexes of Mo(III) with NH_3.

The Tetraammineformatomolybdenum(III) Cation. Tripotassium hexacarbonyl-μ-triol-dimolybdate(0) (0.4 g) was added to a concentrated aqueous ammonia solution (10 ml). The immediate product was a pale yellow solid under a yellow solution. Enough silver tosylate was added to this mixture under agron as a blanketing gas and with stirring to bring the molybdenum to a mean oxidation state of 3. Immediately thereafter a black precipitate formed which was removed by filtration under argon. The pH was adjusted to 2 by HSO_3CF_3 and the solution was further diluted to 400 ml, care being taken to avoid heating above room temperature and to exclude oxygen.

The ion exchange was carried out with the type of column and resin used for the hexaaquomolybdenum(III) cation. The column was washed with 200 ml of water and then with 200 ml of 0.2 *M* HCl to remove $NH_4{}^+$. Some molybdenum-containing species were eluted by the aqueous wash and by the wash with 0.2 *M* HCl. But apart from determining the mean oxidation number of the contained molybdenum, no attempt was made to characterize them. On washing with 0.5 *M* HCl, a species was eluted which we did investigate more thoroughly. The mean oxidation number for molybdenum in the species was found to be 3.1 ± 0.3. No absorption bands were observed in the visible region, and any bands which the species might have in the short wavelength region were obscured by Mo(V). Owing to the high extinction coefficients of Mo(V) at 253 and 293 nm, even a slight contamination by it preempts the spectral region in question. Analysis on several preparations showed the ammonia content to be 4.0 ± 0.8 per Mo.

The dominant form of molybdenum in the solution appears from these results to be a tetraammine-molybdenum(III) complex. From the elution characteristics we infer that the ionic charge is 2+. The only source of complexing anion is the carbon monoxide in the starting material. Titration with $MnO_4{}^-$ showed that 2 reducing equiv for Mo are present in addition to those corresponding to the oxidation of Mo(III) to Mo(VI). We conclude, therefore, that formate is produced in the oxidation of the Mo(0) complex. When account is taken of the facts that oxidation produces a substitution-inert center, Mo(III), and that this center, having lost its propensity for back-donation can now function simply as a Lewis acid, the transformation of CO to $HCO_2{}^-$ is not surprising.

On the basis of the evidence presented, we believe that $[Mo(NH_3)_4(HCO_2)H_2O]^{2+}$ is produced by the preparative procedure outlined, but in low yield (recovery *ca.* 5% based on the amount of carbonyl starting material). It seems likely that diformato species are contained in the earlier wash liquids, particularly in view of the fact that the 0.2 *M* HCl eluate was found to contain Mo in an oxidation state only slightly in excess of 3.

B. Preparation and Characterization of Mo(II) Species. Tetrapotassium Tetrakis(sulfato)dimolybdate(II). About 0.1 g of potassium sulfate was added with stirring to a 20-ml solution of 0.2 *M* $K_4Mo_2Cl_8$ in 0.2 *M* HSO_3CF_3. The solution changed hue, and after about 2 min a pink precipitate had formed. The supernatant solution was colorless or at most a slight greenish yellow. The precipitate was separated by filtration and was washed with two 20-ml portions of re-

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[17] Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 767 (1973).

[18] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

[19] M. Ardon and A. Pernick, *Inorg. Chem.*, **12**, 2484 (1973).

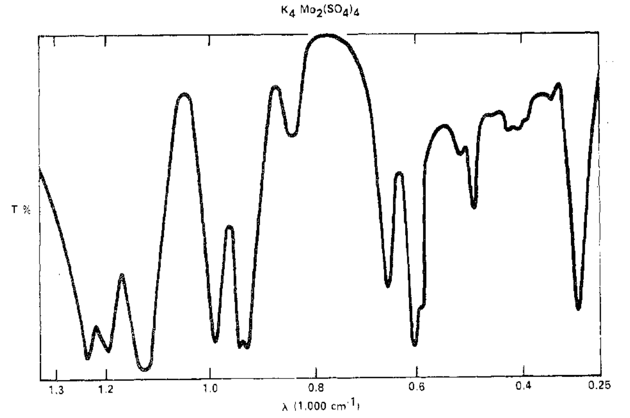

Figure 2. Infrared absorption spectrum of $K_4Mo_2(SO_4)_4$.

distilled water at 0°, with 20 ml of ethanol, and with 20 ml of absolute ether under argon.

The yield was 90%. *Anal.* Calcd for $K_4Mo_2(SO_4)_4$: K, 21.4; Mo, 26.2; SO_4^{2-}, 52.4. Found: K, 21.0; Mo, 25.9; SO_4^{2-}, 52.0.

The solid-state uv-visible spectrum taken for the compound in a pellet shows a band maximum at 519 nm and a stronger one at 232 nm. The compound is diamagnetic.

The structure of the ion $Mo_2(SO_4)_4^{4-}$ in a crystalline solid has been described,[20] and the sulfate ions have been shown to bridge the molybdenum ion. The ir spectrum (*cf.* Figure 2) shows bands at 1234, 1194, 1130-1105, 990, and 944 cm^{-1} ascribable to sulfate. It is consistent with bidentate sulfate being present in the solid.

Compounds Containing $Mo_2(en)_4^{4+}$. In preparing the chloride salt, 0.23 g of $K_4Mo_2Cl_8$ was added to 0.5 ml of ethylenediamine, and while being kept under argon in a closed vessel, the mixture was heated on a steam bath for 30-60 min. During this time, the solid changed from red to orange or brown. The solid was then washed with ethanol followed by ether and was dried under a vacuum.

To recrystallize it, the solid was dissolved in redistilled water, using *ca.* 0.01 g/40 ml. On adding hydrochloric acid to make its concentration about 0.2 *M*, an orange precipitate formed. After three recrystallizations the solid showed the following analysis. *Anal.* Calcd for $Mo_2(C_2H_4NH_2)_4Cl_4$: Mo, 33.4; Cl, 24.7; N, 19.5; C, 16.7; H, 5.6. Found: Mo, 33.3; Cl, 24.4; N, 19.6; C, 16.3; H, 5.3.

In water solution, the compound shows absorption bands at 478 nm (ϵ 483), 360 nm (ϵ 36.4), and 235 nm (ϵ 966) (*cf.* Figure 3).

The mean oxidation number for molybdenum in the chloride salt was found to be 2.0 ± 0.1 and in the *p*-toluenesulfonate salt, 2.05 ± 0.10.

The *p*-toluenesulfonate salt was prepared by using *p*-toluenesulfonic acid in place of hydrochloric acid in the recrystallization procedure described above. As before, the solid was washed with ether and ethanol and then dried under vacuum.

The solution in water gave a spectrum identical with that described for the chloride, except in the uv region where the *p*-toluenesulfonate ion also absorbs.

When a solution of $Mo_2(en)_4Cl_4$ (1×10^{-3} *M*) in 1×10^{-3} *M* HSO_3CF_3 was kept at room temperature over a period of several hours, the color changed from orange-yellow to pink. In more quantitative terms, the strong absorption maximum changed from 478 to 490 nm, a change which indicates aquation. Throughout, the mean oxidation number of Mo remained at 2. When OAc^- is present initially, the absorbance changes are consistent with the acetato complex being formed. The indications are that although $Mo_2(en)_4^{4+}$ in solution undergoes aquation slowly enough to make possible many studies of its properties and reactivity, such studies at room temperature cannot extend beyond *ca.* 30 min without serious complication from aquation.

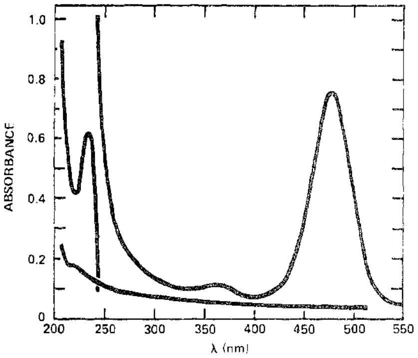

Figure 3. Absorption spectrum of $Mo_2(en)_4^{4+}$. $[Mo_2(en)_4^{4+}] = 1.5 \times 10^{-3}$ *M*; $[HSO_3CF_3] = 1.0 \times 10^{-2}$ *M*; 1-cm cell. Lower curve gives base-line absorption. Absorbance in far-uv region registered on the second decade.

In solution, $Mo_2(en)_4^{4+}$ reacts slowly enough with O_2 to make it possible to work with it without rigorous exclusion of air. Even with Br_2, reaction is slow, on the time scale of many minutes.

On subjecting a solution of $Mo_2(en)_4^{4+}$ to study by cyclic voltammetry, at a sweep rate of 92 mV/sec, a wave is observed at 0.78 V *vs.* sce but the wave is irreversible. This suggests that a major structural reorganization follows rapidly on electron removal. Solid phases containing $Mo_2(SO_4)_4^{3-}$ have been prepared, and the ion has been found[21] to have a molecular framework very similar to that of $Mo_2SO_4^{4-}$.[20] In view of this fact we conclude that $Mo_2(en)_4^{5+}$, which can reasonably be assumed to be the first product of the oxidation of $Mo_2(en)_4^{4+}$, is very labile in solution and readily yields mononuclear Mo(III). It should be noted, however, that there is evidence to suggest that $Mo_2(en)_4^{5+}$ is stable in the solid. In one instance in preparing $Mo_2(en)_4Cl_4$, the material was recrystallized in air. The solid which formed differed from $Mo_2(en)_4Cl_4$ in being bright reddish orange rather than orange. *Anal.* Calcd for $Mo_2(en)_4Cl_5$: C, 15.7; N, 18.4; Mo, 31.6; Cl, 29.2. Found: C, 15.75; N, 17.36; Mo, 32.6; Cl, 29.5.

Some experiments were done oxidizing $Mo_2(en)_4^{4+}$ with Ce(IV) in H_2SO_4 solution. On adding enough Ce(IV) to change the mean oxidation number to 2.5, a large decrease in absorbance (40%) at 478 nm was noted. For net oxidation to 3, 4, and 5 states absorbance decreases of 50, 25, and 17%, respectively, are expected on the conservative assumption that the absorbances of the products at 478 nm are zero. If the conclusion based on cyclic voltammetry that a state such as $Mo_2(en)_4^{5+}$ is unstable in solution is accepted, the results show that the action of Ce(IV) on $Mo_2(en)_4^{4+}$ does form Mo(III) in moderately good yield. This conclusion is supported by the observation that the absorption grows in the region of 360 nm where Mo(III) is known to absorb (if en is coordinated to Mo(III), the band maximum is expected at shorter λ than is the case for the aquo ion). On continuing to add Ce-

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(20) C. L. Angell, F. A. Cotton, B. A. Frenz, and T. R. Webb, *J. Chem. Soc., Chem. Commun.*, 399 (1973).

(21) F. A. Cotton, B. A. Frenz, and T. R. Webb, *J. Amer. Chem. Soc.*, **95**, 4431 (1973).

(IV), production of Mo(III) is less efficient, and a greater proportion of the higher oxidation state Mo(V) is formed.

None of the work we have done settles the question of the disposition of the ethylenediamine molecules around the dimolybdenum ion. Space-filling models suggest that they cannot bridge the Mo(II) ions, and on this basis we presume that each pair occupies the equatorial positions around a Mo(II) ion. The infrared spectrum of the chloride shows bands in the region expected for ethylenediamine in the gauche configuration.[22]

Dichlorobis(2,2′-dipyridylmolybdenum(II). Tetrapotassium octachlorodimolybdate(II) (0.12 g) was dissolved in 10 ml of deaerated methanol. To this solution was added 10 ml of deaerated methanol containing 1.5 g of 2,2′-dipyridyl and 1 ml of concentrated HCl. The mixture was kept under argon for 5 hr. During this time the solution was somewhat reduced in volume, and a dark purple precipitate began to form. After cooling the mixture to 0°, the crystals were removed by filtration, were washed by methanol and ethanol, and were dried *in vacuo*. *Anal.* Calcd for $Mo_2C_{24}H_{20}N_4Cl_4$: Mo, 29.7; N, 8.67; C, 37.2; H, 2.48; Cl, 22.0. Found: Mo, 29.6; N, 8.82; C, 37.5; H, 2.74; Cl, 22.02.

The solid is insoluble in water, ethanol, and methanol but slightly soluble in acetone. Efforts to prepare a material containing a higher proportion of 2,2′-dipyridyl to Mo than is present in the 1:1 compound described failed. This failure may be due to a peculiar stability of the 1:1 species as a solid.

The Aquodimolybdenum(II) Cation. Further work has been done on the ion to settle the matter of its absorption spectrum. The extinction coefficients for the long-wavelength bands as reported earlier[2] are definitely in error as suggested to us by Ardon.[14] Redetermination on a solution prepared by adding $Ba(CF_3SO_3)_2$ in slight excess to $K_4Mo_2(SO_4)_4$ dissolved in 0.01 *M* HCF_3SO_3 and filtering to remove $BaSO_4$ showed a band maximum at 504 nm (ϵ 337 M^{-1} cm^{-1}) and a weaker band at 370 nm (ϵ ~40 M^{-1} cm^{-1}) as shown in Figure 4. The positions of the band maxima have proved to be reproducible in a large number of runs. There is still some question about the extinction coefficient for the band at 370 nm. Though there is an intrinsic band for $Mo_2{}^{4+}$(aq) here, a product of the oxidation absorbs in the same region and has a higher extinction coefficient.

In the experiments described it was shown that sulfate ion had been removed completely and in the redeterminations the mean oxidation number for Mo(II) was 2.0 within experimental error.

The error in the earlier measurements of ϵ has been traced to having inadvertently used for analysis a solution different from that in which the absorption spectrum was taken. But there is also the matter of the wavelength discrepancy to be concerned about. Our more recent experience indicated that solutions which have suffered partial oxidation can show a shift of the band at 504 nm to shorter wavelengths.

The purpose of resorting to $K_4Mo_2(SO_4)_4$ to produce $Mo_2{}^{4+}$(aq) is to rid the solution of chloride ion which might interfere in studies, say, of oxidation to the 3+ state. The method is preferred to cation-exchange separation because, owing to the high charge on the ion, it is difficult to obtain by ion exchange except in dilute solution. For many purposes, however, $Mo_2{}^{4+}$(aq) could be used in the presence of Cl^-, and some experiments were done to learn how readily Cl^- is lost from $Mo_2Cl_8{}^{4-}$.

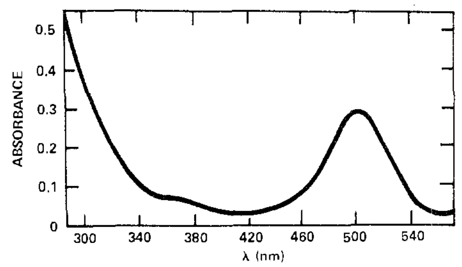

Figure 4. Absorption spectrum of $Mo_2{}^{4+}$(aq). $[Mo_2{}^{4+}] = 8.3 \times 10^{-4}$ *M*; $[HSO_3CF_3] = 1.0 \times 10^{-3}$ *M*; 1-cm cell.

A solution was prepared containing 0.01 *M* $K_4Mo_2Cl_8$ and 0.1 *M* HSO_3CF_3. It was immediately placed on a column containing Sephadex strongly acidic cation resin which was at 5°. The column was then washed with water at 5° until the eluate gave no precipitate with silver ion. The total eluate was collected and analyzed for chloride ion. In 20 experiments this gave a value of 3.0 ± 0.2 chlorides per molybdenum atom. In several of these experiments the red band on the column was then eluted with 0.5-1.0 *M* sodium *p*-toluenesulfonate at a pH of 2. The ratio of chloride to molybdenum in the eluted material varied from 1:1 to 1:6. In the experiment in which a 1:6 ratio was found a brown band was left on the column; the missing chloride ion was probably present in this band. The species eluted having a Mo-Cl ratio of 1:1 showed a band maximum at 512 nm with ϵ 3.4×10^2 M^{-1} cm^{-1}. The mean oxidation number of Mo was determined as 2.0 ± 0.1 The results are consistent with the idea that three chloride ions per $Mo_2Cl_8{}^{4-}$ are lost rapidly when $K_4Mo_2Cl_8$ is dissolved in a solution of a noncomplexing acid. The conclusion is supported by the fact that the solution, even when freshly made up, shows an absorption maximum at 515 nm, rather than at 522 nm as is the case for the solid.

A portion of a solution made up as described in the preceding paragraph was kept for 1 month under N_2. During this time, the mean oxidation number of the molybdenum had increased to 2.3, and the long-wavelength band maximum had moved to 500 nm. The uv region of the spectrum was obscured by strong absorption arising, we believe, from Mo(V).

The aquodimolybdenum(II) cation is apparently a route to complexes of Mo(III) by appropriate oxidation processes. In one experiment a solution of $Mo_2{}^{4+}$(aq) (0.001 *M*) in HSO_3CF_3 was oxidized with enough $I_3{}^-$ to raise the average oxidation of Mo to 3. The yellow solution which formed was placed on a cation-exchange resin. This was first washed with 0.2 *M* HSO_3CF_3. The major species on the resin was readily eluted from the column with 1 *M* HSO_3CF_3 and thus appears to carry an ionic charge of 2+ per unit. A strong absorption band began to set in at about 360 nm and was probably ascribable to I^- to Mo(III) charge transfer. The solution gave a positive test for I^-, and we therefore appear to have MoI^{2+} in hand.

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Registry No. $Mo(H_2O)_6{}^{3+}$, 34054-31-4; K_3MoCl_6, 13600-82-3; $Mo(NH_3)_3Cl_3$, 51806-32-7; $K_3[(CO)_3Mo(OH)_3Mo(CO)_3]$, 33461-60-8; $[Mo(NH_3)_4(HCO_2)H_2O]^{2+}$, 51806-33-8; $K_4Mo_2(SO_4)_4$, 51806-35-0; $K_4Mo_2Cl_8$, 25448-39-9; en, 107-15-3; $Mo_2(en)_4Cl_4$, 51806-36-1; $Mo(en)_4Cl_5$, 51806-37-2; 2,2′-$NC_5H_5C_5H_5N$, 366-18-7; $Mo_2C_{20}H_{16}N_4Cl_4$, 51838-67-6.

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[22] K. Nakamoto, "Infared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.