equilibrium product, it is not formed at an appreciable rate at $\leq 875°$. The reactions observed here are somewhat analogous to those found in the Nb_6Cl_{14}–Nb–SiO_2 system where $NbOCl_3$ is the intermediate and the oxygen formed first dissolves in the metal but ultimately produces NbO.[18] In the presence of the condensed lower iodides the net reaction

$$3SiO_2 + {}^{52}/_{15}Nb_6I_{11} = Nb_5Si_3 + 6NbOI_2 + {}^{49}/_{15}Nb_3I_8 \quad (7)$$

involves only solid phases. Actually still another transport equilibrium is probably involved for Nb_5Si_3 since it is not uniformly distributed on the walls but is more predominant on the hotter parts of the glass. Such presumably involves SiI_4 and might be

$$Nb_5Si_3(s) + {}^{27}/_2I_2(g) = 5NbI_3(g) + 3SiI_4(g) \quad (8)$$

Unfortunately there are insufficient thermodynamic data available for the niobium iodides to judge further the plausibility of these reactions. Presumably the higher pressures that arose in the total-pressure studies once Nb_5Si_3 had been formed resulted from the $NbOI_3$ and SiI_4 contributions, and the erratic character of the pressures observed was caused by irregular contributions of convection to the otherwise steady-state diffusion processes.

According to the present study the vapor species NbI_3 would appear to be of principal importance in the purification of niobium metal by the iodide process. In one study of this method[21] a definite maximum in the filament growth rate occurred at 450–475° when the temperature of the feed metal was varied at a constant filament temperature of 1250°. On a further increase in the feed temperature the growth rate first decreased up to about 550° and then increased rapidly with increasing temperature up to at least 750°. Rolsten[22] observed a somewhat similar behavior with his growth rate–feed temperature curve, but this was displaced to lower temperatures by about 75–100°, which probably reflects the difficulty in accurately measuring the true feed metal temperature. Since the initial oxidation product of excess metal at 400–500° appears to be NbI_3 rather than a lower iodide,[2] the first increase in the growth rate probably results from the increasing volatility of NbI_3 and this then decreases at higher temperatures as NbI_3 is increasingly reduced and decomposed to the much less volatile Nb_3I_8. However, as the temperature approaches 600° the growth rate rises again as, according to the present study, gaseous NbI_3 is produced by the incongruent vaporization of Nb_3I_8, and this results in the steady increase in the growth rate up to at least 750°. Even at 800–900° the reaction of Nb_3I_8 with metal to produce Nb_6I_{11} is extremely slow, presumably because of the structural complexity of the transformation, so the equilibrium phase is probably not involved in the process at these temperatures.

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Tetracyano Complexes of Molybdenum(IV)

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Methods are presented for the preparation and identification of the following molybdenum(IV) compounds: red-violet $K_4[MoO_2(CN)_4]\cdot 6H_2O$, tan $K_4[MoO_2(CN)_4]$, blue $K_3[MoO(OH)(CN)_4]$, green $K_2[Mo(OH)_2(CN)_4]$, and black $Mo(OH)_2(CN)_2\cdot H_2O$. The infrared spectra, which are particularly useful for identification, are discussed. The acid dissociation constants for $MoO(OH)(CN)_4{}^{3-}$ and $Mo(OH)_2(CN)_4{}^{2-}$ at 25° are, respectively, 2.4×10^{-13} and 1.05×10^{-10}. A new compound, $K_6[Mo^{IV}{}_2Mo^{VI}(CN)_8O_6]\cdot 2H_2O$, is reported.

Tetracyano complexes of molybdenum(IV) have been known for a considerable time. A compound, described as red or red-violet, has been prepared by treating various Mo(V) compounds with KCN and KOH.[1–9] Photochemical decomposition of $Mo(CN)_8{}^{4-}$ can be made to yield the same product.[10,11] All procedures used have in common the isolation of the compound from a strongly basic solution. Recent crystallographic work[11–13] has demonstrated that this compound contains the *trans*-dioxotetracyanomolybdate(IV) anion and is best formulated as $K_4[MoO_2(CN)_4]\cdot 6H_2O$. The anhydrous compound $K_4[MoO_2(CN)_4]$ was first prepared by Steele.[14]

The red-violet compound dissolves in water to give

(1) E. Pechard, *Compt. Rend.*, **118**, 804 (1894).
(2) K. von der Heide and K. A. Hofmann, *Z. Anorg. Allgem. Chem.*, **12**, 277 (1896).
(3) A. Rosenheim and M. Koss, *ibid.*, **49**, 148 (1906).
(4) A. Rosenheim, A. Garfunkel, and F. Kohn, *ibid.*, **65**, 166 (1909).
(5) G. A. Barbieri, *Atti Accad. Nazl. Lincei, Mem. Classe Sci. Fis. Mat. Nat., Sez. I*, **25**, 775 (1916).
(6) W. R. Bucknall and W. Wardlaw, *J. Chem. Soc.*, 2981 (1927).
(7) E. Crepaz, *Gazz. Chim. Ital.*, **58**, 391 (1928).
(8) W. F. Jakob and E. Turkiewicz, *Roczniki Chem.*, **11**, 569 (1931).
(9) Z. Jakob, *ibid.*, **31**, 681 (1957).
(10) O. Collenberg, *Z. Anorg. Allgem. Chem.*, **136**, 245 (1924).
(11) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, **6**, 1943 (1967).
(12) S. J. Lippard, H. Nozaki, and B. J. Russ, *Chem. Commun.*, **3**, 119 (1967).
(13) V. W. Day and J. L. Hoard, *J. Am. Chem. Soc.*, **90**, 3374 (1968).
(14) M. C. Steele, *Australian J. Chem.*, **10**, 404 (1957).

a blue solution, and indeed, from solutions less alkaline than those yielding the red-violet compound, blue compounds have been isolated.[15-18] A variety of formulas have been suggested for these compounds, but the recent evidence[11-18] indicates that the six-coordinate formulations are correct rather than the eight-coordinate formulations.

The following investigation was made in an attempt to clarify the nature of the blue hydrolysis products. Improved methods for the preparation, analysis, and characterization of the hydrolysis products have been developed. Our results are, in general, consistent with the conclusions of Lippard and Russ,[11] but the infrared spectra of our compounds vary in some respects from those reported by Lippard and Russ. There is, of course, the possibility that our compounds are not the same as theirs, as different synthetic methods were used.

Experimental Section

Red-Violet $K_4[MoO_2(CN)_4]\cdot 6H_2O$.—This compound was prepared using a variation of the method described by Jakob.[9] After reduction of ammonium paramolybdate with hydrazine in concentrated HCl, $MoO(OH)_3$ was precipitated with ammonium hydroxide. Treatment with aqueous KCN and KOH yielded a clear, deep blue solution. Addition of 50% KOH and cooling caused crystallization of the red-violet compound. Purification was accomplished by redissolving the compound in a small amount of water and subsequent dropwise addition of a 50% KOH solution, The yield, based on ammonium paramolybdate, was 40%. *Anal.* Calcd for $K_4[MoO_2(CN)_4]\cdot 6H_2O$: K, 31.45; Mo, 19.35. Found: K, 31.97; Mo, 19.27.

The red-violet compound dissolves in water to give a blue solution, and upon evaporation under reduced pressure at 70° the red-violet crystals reappear. The red-violet compound loses water easily *in vacuo* over drying agents, turning tan in the process. *In vacuo* at room temperature over KOH–$Mg(ClO_4)_2$, 20.3% of the weight (corresponding to 5.6 mol of water/mol of complex) was lost. *In vacuo* at 55° over $Mg(ClO_4)_2$, 20.8% of the weight (corresponding to 5.8 mol of water) was lost.

Tan $K_4[MoO_2(CN)_4]$.—This compound can be prepared simply from the red-violet complex by dehydration as described above. The dehydration can be accomplished faster and somewhat more completely at elevated temperatures, but even at 100° small amounts of water remain in the sample. Steele[14] reports that this compound "is very soluble in water giving a yellowish brown solution." We have prepared the compound several times, and dried it under a variety of conditions. It is very soluble in water and in all cases gives a blue solution. The blue solution is apparently identical with that formed when the red-violet solid is dissolved in water. The tan compound turns blue upon exposure to the atmosphere, but it can be kept indefinitely *in vacuo* over $CaCl_2$, KOH, or $Mg(ClO_4)_2$. *Anal.* Calcd for $K_4[MoO_2(CN)_4]$: K, 40.21; Mo, 24.75; C, 12.37; N, 14.43; H, 0.00. Found: K, 39.76; Mo, 24.22; C, 12.37; N, 13.58; H, 0.32.

Blue $K_3[MoO(OH)(CN)_4]$.—Small portions of Dowex 50W-X4 ion-exchange resin in the H^+ form were added to a solution of 25 g of red-violet tetracyano complex in 60 ml of water until the pH was 11. After removal of the resin by filtration, a blue compound was precipitated with ethanol. The compound was washed with acetone and dry ether and dried at 100° *in vacuo* over KOH–$Mg(ClO_4)_2$ for 48 hr. It dissolves in water to give a blue solution. *Anal.* Calcd for $K_3[MoO(OH)(CN)_4]$: K, 33.43; Mo, 27.43; C, 13.71; N, 16.00; H, 0.29. Found: K, 33.36; Mo(t), 28.16; Mo(IV), 28.24; C, 15.07; N, 15.87; H, 0.22.

Green $K_2[Mo(OH)_2(CN)_4]$.—Small portions of Dowex 50W-X4 ion-exchange resin in the H^+ form were added to a solution of 25 g of red-violet tetracyano complex in 60 ml of water, until the pH was 7.0. After removal of the resin by filtration, a dark green oil separated upon addition of ethanol. After decantation of the supernatant solution the oil was made to crystallize with acetone. The green solid was washed with acetone and dry ether and dried at 100° *in vacuo* over KOH–$Mg(ClO_4)_2$ for 48 hr. *Anal.* Calcd for $K_2[Mo(OH)_2(CN)_4]$: K, 25.00; Mo, 30.77; C, 15.38; N, 17.95; H, 0.64. Found: K, 25.77; Mo(t), 34.85; Mo(IV), 30.42; C, 18.87; N, 17.53; H, 0.77.

The compound is hygroscopic and soluble in water. A concentrated solution in water is green but turns blue upon addition of more water. This change is reversible; upon evaporation under reduced pressure the blue solution turns green and the green solid reappears. We have been unable to precipitate a blue $K_2[Mo(OH)_2(CN)_4]$ compound by treating the dilute blue solution with ethanol. However, the dark green oil thus produced transforms itself upon prolonged standing, while still covered with ethanol, into a blue solid. The ir spectrum of this blue solid is identical with that of $K_6Mo^{IV}_2Mo^{VI}(CN)_8O_6\cdot 2H_2O$, to be described later.

Following the above procedure but using pH 7.5 and 8.5 rather than 7.0, preparations were obtained. In both cases green solids similar to the one described above were produced. Ir spectral studies indicate, however, that with increasing pH an increasing amount of $K_3[MoO(OH)(CN)_4]$ is present in the preparation. This is not unexpected.

Jakob[9] reported the isolation of a blue compound of formula $K_2[Mo(OH)_2(CN)_4]$ from aqueous solutions after disproportionation of Mo(V). Following the method described[9] we obtained a blue solid. The preparation was washed with alcohol, acetone, and dry ether and dried at room temperature *in vacuo* over KOH–$Mg(ClO_4)_2$. It dissolves in water to give a blue solution. The pH of a 0.025 *M* solution is 10.5. Its diamagnetism indicates the absence of Mo(V). On the basis of the analytical data, the acid titration of the material, and the ir spectrum, it can be concluded that our material is a mixture of $K_3[MoO(OH)(CH)_4]$ and K_2MoO_4.

Anal. Found: K, 32.99; Mo(t), 31.60; Mo(IV), 20.07; C, 11.78; N, 12.28; H, 0.37.

Blue-Purple $Cd(H_2O)_6[Mo(OH)_2(CN)_4]$.—A compound of this color and formula has been reported by Jakob and Michalewicz.[16] When an aqueous solution of $CdCl_2$ was added to a blue aqueous solution of green $K_2[Mo(OH)_2(CN)_4]$, a blue-purple precipitate formed quickly. The precipitate was washed with acetone and dry ether and dried at room temperature *in vacuo*. The compound is insoluble in water. Upon drying *in vacuo* at 100° it loses water, and the color changes from blue-purple to brown-green. The ir spectrum of the dried sample matches that of green $K_2[Mo(OH)_2(CN)_4]$.

Black $Mo(OH)_2(CN)_2\cdot H_2O$.—The compound $Mo(OH)_2(CN)_2\cdot xH_2O$, described by Jakob and Michalewicz,[15] was prepared by treating a water solution of the red-violet complex with 6 *M* HCl. After the formation of a green gellike precipitate, more water was added and the reaction mixture was heated on a steam bath for 30 min. The dark green precipitate was removed by filtration and thoroughly washed with water. The compound was dried at room temperature *in vacuo* over KOH–$Mg(ClO_4)_2$ during which process it turned into a fine black powder. The compound is insoluble in water and does not contain any potassium. A 30-g sample of the red-violet complex yielded 11.5 g of $Mo(OH)_2(CN)_2\cdot H_2O$. *Anal.* Calcd for $Mo(OH)_2(CN)_2\cdot H_2O$: Mo, 48.00; C, 12.00; N, 14.00; H, 2.00. Found: Mo, 46.51; C, 16.58; N, 12.21; H, 2.30.

Blue $K_6[Mo^{IV}_2Mo^{VI}(CN)_8O_6]\cdot 2H_2O$.—Following the method described by Bucknall and Wardlaw,[6] a blue preparation was obtained from a water solution of the red-violet complex by repeated precipitation with methanol until the supernatant

(15) W. F. Jakob and C. Michalewicz, *Roczniki Chem.*, **12**, 576 (1932).
(16) W. Jakob and Z. Jakob, *ibid.*, **36**, 593 (1962).
(17) A. W. Adamson and J. R. Perumareddi, *Inorg. Chem.*, **4**, 247 (1965).
(18) W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 872 (1959).

solution was neutral to litmus. The preparation was washed with acetone and dry ether and dried at room temperature *in vacuo* over KOH–$Mg(ClO_4)_2$. Upon drying at 100° *in vacuo* for 64 hr 3.17% water was lost. This preparation is definitely not the compound $K_3[Mo(OH)_3(H_2O)(CN)_4]$ prepared by Bucknall and Wardlaw. It contains Mo(VI) as well as Mo(IV). It dissolves in water to give a blue solution. The pH of a 0.025 *M* solution is 8.4. The ir spectrum shows no evidence of MoO_4^{2-} nor of identified tetracyano complexes of Mo(IV). The spectrum and the Mo(t):Mo(IV) ratio remains unchanged upon repeated precipitation with either methanol or ethanol. This suggests the material is a compound rather than a mixture. *Anal.* Calcd for $K_6[Mo^{IV}_2Mo^{VI}(CN)_8O_6]\cdot 2H_2O$: K, 27.2; Mo(t), 32.2; Mo(IV), 21.5; C, 11.13; N, 13.01; H, 0.47. Found: K, 28.21; Mo(t), 32.07; Mo(IV), 21.71; C, 11.14; N, 12.16; H, 0.50.

Analytical Methods.—Molybdenum(IV) in water-soluble compounds was determined by potentiometric titration following the procedure reported by Mikhalevich and Litvinchuk[19] for corresponding tungsten compounds. To 5 ml of 0.1 *N* $K_3Fe(CN)_6$ is added 40 ml of 0.1 *N* KOH, and this solution is titrated with a 0.1 *M* solution of the complex. In this process Mo(IV) is oxidized to Mo(VI) in one step. The titration was followed potentiometrically using a Beckman research pH meter with a platinum electrode. Reversal of the procedure, *i.e.*, titrating the Mo(IV) complex solution with the $K_3Fe(CN)_6$ solution, is not sufficiently reproducible for purposes of analysis.

For the determination of molybdenum(IV) in water-insoluble compounds, or determination of total molybdenum in any sample, the following procedure was used. The sample was digested over a period of 3 hr with concentrated sulfuric acid, thus bringing all molybdenum to the VI state while at the same time removing all cyanide. The molybdenum was then reduced to the III state in a Jones reductor, and the resulting solution was titrated under nitrogen with $KMnO_4$ oxidizing all Mo(III) to Mo(VI).

Potassium was determined gravimetrically as potassium tetraphenylborate.[20] Microanalyses for C, H, and N were performed by Galbraith Laboratories, Knoxville, Tenn. Values for C and N were somewhat erratic, a behavior which has been observed by other workers for these and similar compounds.[11]

Potentiometric Titration with Acid.—Potentiometric titrations with acid were performed with a Beckman research pH meter, using a glass electrode. In Figure 1 is shown the result of titrating a 0.025 *M* solution of the red-violet complex with 0.10 *M* HCl. Three inflection points are evident in this graph, corresponding to the addition of 1, 2, and 4 mol of H^+/mol of complex.

The first inflection point, at pH 10.95, corresponds to the formation of $MoO(OH)(CN)_4^{3-}$. The second inflection point, at pH 7.50, corresponds to the formation of $Mo(OH)_2(CN)_4^{2-}$. Samples of other compounds show a behavior consistent with this graph, but differing in the starting point. For example, a 0.025 *M* solution of blue $K_3[MoO(OH)(CN)_4]$ has a pH of 10.85, and titration with acid gives a sharp inflection point at a pH of 7.25 after the addition of one H^+ per complex ion.

The inflection point that appears in Figure 1 corresponding to the addition of four H^+ ions does not appear in titration of all samples. In this part of the curve the pH is apparently dependent on time of titration in addition to the concentration of the reactants. This, plus other evidence, indicates that the processes occurring at pH ≤ 7 are more complicated than the mere addition of protons. Decomposition, with loss of HCN, is probably the most significant complicating reaction, with oxidation by air being a smaller complication.

Physical Measurements.—Magnetic susceptibility measurements were made with a Gouy-type apparatus, using $Hg[Co(CNS)_4]$ as a standard. Measurements were made on the seven compounds and the one mixture whose ir spectra are shown in Figures 2 and 3. In all cases the samples were found to be diamagnetic. The susceptibilities corresponded to the values calculated by use of Pascal's constants, thus indicating the absence of any paramagnetism.

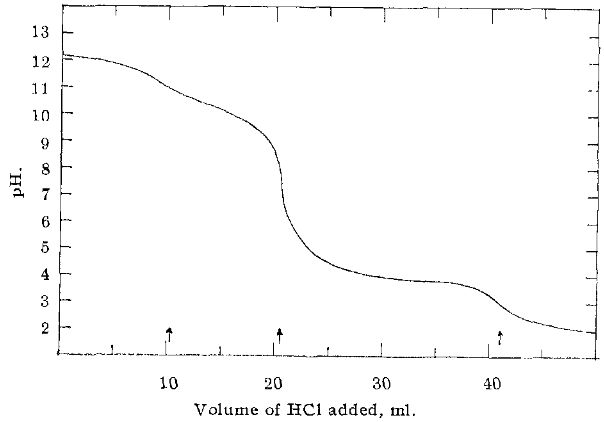

Figure 1.—Titration of 0.025 *M* $K_4[MoO_2(CN)_4]\cdot 6H_2O$ with hydrochloric acid.

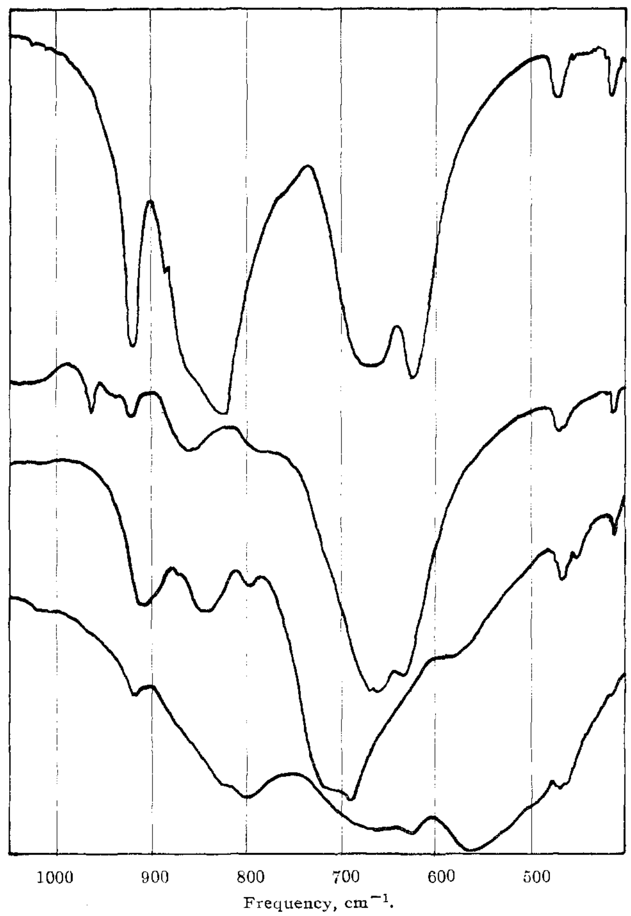

Figure 2.—Infrared spectra of (from top to bottom) material prepared by method of Jakob: $K_3[MoO(OH)(CN)_4]$, $K_4[MoO_2(CN)_4]$, and $K_4[MoO_2(CN)_4]\cdot 6H_2O$.

Measurements of the infrared spectra were made on a Perkin-Elmer 337 spectrophotometer. Samples for infrared measurement were prepared by the KBr-pellet technique, operations being performed in a drybox to the extent possible.

Absorption spectra in the region 210–1000 mμ were obtained with a Cary Model 14 spectrophotometer. In Table I are presented data on the visible spectra obtained from measurements at pH's on solutions of $K_4[MoO_2(CN)_4]\cdot 6H_2O$ at a concentration of 0.015 *M*. At this concentration a green precipitate formed

(19) K. N. Mikhalevich and V. M. Litvinchuk, *Zh. Neorgan. Khim.*, **9**, 2391 (1964); *Russ. J. Inorg. Chem.*, **9**, 1293 (1964).

(20) H. Flaschka and A. J. Barnard, *Advan. Anal. Chem. Instr.*, **1**, 1 (1960).

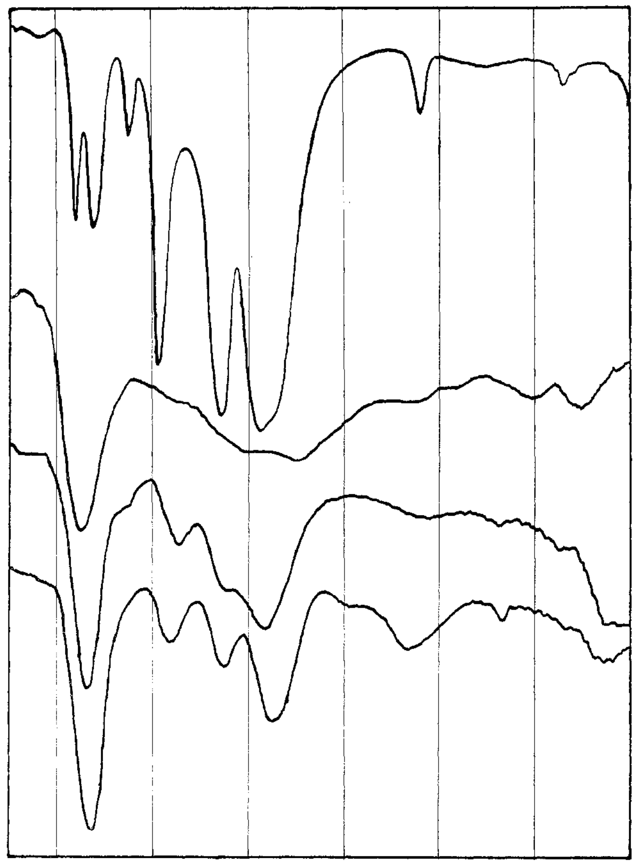

Figure 3.—Infrared spectra of (from top to bottom): $K_6[Mo^{VI}_2Mo^{VI}(CN)_8O_6] \cdot 2H_2O$, $[Mo(OH)_2(CN)_2] \cdot H_2O$, $Cd[Mo(OH)_2(CN)_4]$, and $K_2[Mo(OH)_2(CN)_4]$.

TABLE I
VISIBLE SPECTRA OF 0.015 M $K_4[MoO_2(CN)_4] \cdot 6H_2O$ SOLUTIONS

pH	λ_{max}, mμ	Absorbancy[a]	F_{II}[b]	F_{III}[b]	F_{IV}[b]	Medium
4.97	610	0.71	...	...	...	Acetate buffer
6.26	612	0.71	...	...	...	Acetate buffer
7.10	609	0.71	1.00	0.00	0.00	Phosphate buffer
8.26	616	0.68	0.98	0.02	0.00	Ammonia buffer
9.23	621	0.67	0.88	0.12	0.00	Ammonia buffer
10.28	622	0.68	0.38	0.62	0.00	Ammonia buffer
11.67	596	0.68	0.02	0.90	0.08	Na_2CO_3
12.76	595	0.67	0.00	0.48	0.52	KOH
13.62	594	0.68	0.00	0.11	0.89	KOH

[a] 1-Cm cell. [b] F is estimated fraction of Mo present in a particular form: II is $Mo(OH)_2(CN)_4^{2-}$, III is $MoO(OH)(CN)_4^{3-}$, and IV is $MoO_2(CN)_4^{4-}$.

just below pH 5. In Table II are presented data on the ultraviolet spectra obtained with solutions 6×10^{-5} M in the same compound.

Discussion

Preparation and Identification of Compounds.—If one assumes that the red-violet solid contains the complex ion $MoO_2(CN)_4^{4-}$, the titration curve (Figure 1) is readily interpreted in terms of the formation of $MoO(OH)(CN)_4^{3-}$ and $Mo(OH)_2(CN)_4^{2-}$. The titration behavior also suggested that isolation of these complexes would be most easily achieved by adjusting the pH to the end point values, and the procedures leading to the blue $K_3[MoO(OH)(CN)_4]$ and green $K_2[Mo(OH)_2(CN)_4]$ were so designed. The argument may be made that the procedure is so designed that the solution contains K, Mo, and CN^- in a certain ratio and if crystallization removes them completely, whether as one compound or as a mixture, the ratio must be maintained in the solid. Hence, the analytical data alone cannot settle the question of whether these solids are compounds or mixtures.

TABLE II
ULTRAVIOLET SPECTRA OF 6.0×10^{-5} M $K_4[MoO_2(CN)_4] \cdot 6H_2O$ SOLUTIONS

pH	λ_{max}, mμ	Absorbancy	F_{II}[c]	F_{III}[c]	F_{IV}[c]	Medium
1.18	295	0.85[a]	...	...	...	HCl
2.09	295	0.57[a]	...	...	...	Chloroacetate buffer
2.82	299	1.75[a]	...	...	...	Chloroacetate buffer
3.80	299	0.13[b]	...	...	...	Acetate buffer
4.92	299	0.12[b]	...	...	...	Acetate buffer
6.13	299	0.08[b]	...	...	...	Acetate buffer
6.97	226	0.52[b]	1.00	0.00	0.00	Phosphate buffer
8.19	226	0.58[b]	0.99	0.01	0.00	Ammonia buffer
9.24	226	0.75[b]	0.87	0.13	0.00	Ammonia buffer
10.27	226	0.58[b]	0.39	0.61	0.00	Ammonia buffer
12.70	226	0.37[b]	0.00	0.51	0.49	KOH
13.61	226	0.29[b]	0.00	0.11	0.89	KOH

[a] 10-Cm cell. [b] 1-Cm cell. [c] F is estimated fraction of Mo present in a particular form: II is $Mo(OH)_2(CN)_4^{2-}$, III is $MoO(OH)(CN)_4^{3-}$, and IV is $MoO_2(CN)_4^{4-}$.

In deciding whether a given sample is a mixture or a pure compound the following observations were considered: comparison of the total Mo with the amount of Mo(IV) as determined by the ferricyanide titration, the titration behavior with HCl, and the infrared spectrum.

The solutions show some sensitivity to air oxidation, although this is not a marked effect as long as pH ≥ 8. Aqueous solutions of $K_2[Mo(OH)_2(CN)_4]$ are subject to air oxidation over extended periods leading to the formation of brown, insoluble $MoO(OH)_3$. This material is removed easily by filtration so that it provides no difficulty in preparative procedures for the Mo(IV) complexes. When in contact with alcohol solutions, $K_2[Mo(OH)_2(CN)_4]$ is slowly oxidized to the blue compound formulated as containing both Mo(IV) and Mo(VI). The difficulty in preparing pure $K_2[Mo(OH)_2(CN)_4]$ arises from a combination of factors. The pH must be close to 7 to reduce the amount of $MoO(OH)(CN)_4^{3-}$, but at this pH the system has an increased sensitivity to air oxidation.

We have made no attempts to prepare compounds as products of the photochemical decomposition of solutions of $Mo(CN)_8^{4-}$. There is agreement[16,17] that the final product in solution is a blue tetracyano complex of Mo(IV). On the basis of the results reported here, the specific anion(s) in such a solution will be dependent mainly on the pH (as long as pH ≥ 8), and the solid isolated will vary with the procedure used.

Infrared Spectra.—The ir spectra have been particularly valuable in recognizing the various complexes. All compounds display sharp, closely spaced peaks at about 2080 cm^{-1}, characteristic of C≡N stretching. The region 400–1100 cm^{-1}, in which bands characteristic of Mo—O bonds appear, is more useful for identification purposes. In Figures 2 and 3 are shown the spectra of solids which are considered to be reasonably pure compounds. Our observations and conclusions are in some respects different from those of Lippard and Russ,[11] who observed the spectra in the 4000–650-cm^{-1} region using Nujol mulls.

A broad band at about 700 cm^{-1}, with a shape suggesting at least two unresolved peaks, is characteristic of the $MoO_2(CN)_4^{4-}$ ion. This band appears distinctly in the spectrum of the tan compound, but it is obscured in the spectrum of the red-violet compound by even broader bands which are attributed to the librational motion[21] of the water molecules in the lattice. From measurements on the hydrate, but not on the anhydrous compound, Lippard and Russ[11] assigned the broad band at 800 cm^{-1} to the Mo–O stretch. Both of our compounds show peaks of lower intensity at 1370 and 1420 cm^{-1}. Presumably these are combination bands related to the bands at 700 cm^{-1}.

The bands at 700 cm^{-1} are attributed to the Mo–O stretch because of consistency with the metal–oxygen stretches reported for the compounds $K_2[OsO_2(CN)_4]$[22] and $K_3[ReO_2(CN)_4]$.[23] In these three similar complexes the sequence of frequencies should be determined by the variation in the oxidation state. The expected order of frequencies would be: Os(VI) > Re(V) > Mo(IV). Since the first two frequencies are 830 and 780 cm^{-1}, respectively, a value of 700 cm^{-1} for the Mo(IV) complex is reasonable. One difficulty accompanies this assignment. If the tan compound retains the *trans* O–Mo–O structure[11–13] present in the red-violet compound, the appearance of two bands at 700 cm^{-1} is unexpected. Perhaps dehydration has caused rearrangement to the *cis* O–Mo–O structure.

The broad-band characteristic of $MoO(OH)(CN)_4^{3-}$ appears at somewhat smaller frequencies, with a shape suggesting at least two unresolved peaks. It is attributed to the Mo–O stretch. The Mo–OH stretching frequency would be expected to appear at a much smaller frequency than the Mo–O stretch. For example, in osmium(VI) complexes[22] the Os–O band appears in the 800–870-cm^{-1} region, while the Os–OH band appears in the 500–530-cm^{-1} region. On this basis we assume that the Mo–OH stretch occurs at a frequency less than 400 cm^{-1}, outside the region investigated. Lippard and Russ[11] assigned a band at 921 cm^{-1} as the Mo–O stretching frequency for a compound formulated as $K_3[MoO(OH)(CN)_4]\cdot 2H_2O$. None of our compounds has such a band as a major feature of the spectrum. It is not clear how their compound is related to the ones we have prepared.

A peak at 965 cm^{-1} is characteristic of the compounds that are formulated as salts containing $Mo(OH)_2(CN)_4^{2-}$. This absorption is attributed to Mo–O–H deformation. This assignment is consistent with the evidence for such a band in the region 920–1000 cm^{-1} in certain Ru complexes,[24] at 1050–1090 cm^{-1} in some Os(V) complexes,[22] and at 960–1010 cm^{-1} for Re(V) complexes.[25] The 965-cm^{-1} peak falls in the region characteristic of Mo–O bonds in Mo(V) complexes,[26–28] but if the compounds contain mononuclear Mo(V) complexes, they would be paramagnetic, which they are not. The three peaks in the region 700–900 cm^{-1} are probably due to an impurity to be mentioned below.

Also shown in Figure 2 is the spectrum of the material prepared according to the method of Jakob.[9] Analysis indicated the sample contained both Mo(IV) and Mo(VI). The infrared spectrum verifies that it is a mixture; the band in the 600–700-cm^{-1} region is characteristic of $MoO(OH)(CN)_4^{3-}$, and that in the 800–900-cm^{-1} region is characteristic[29] of MoO_4^{2-}. In addition, there is a band at 920 cm^{-1}, which may correspond to the substance reported by Lippard and Russ[11] as $K_3[MoO(OH)(CN)_4]\cdot 2H_2O$.

Shown in Figure 3 is the spectrum of a material which appears to be a compound containing both Mo(IV) and Mo(VI). The analysis of this material corresponds well to the formula $K_6[Mo^{IV}_2Mo^{VI}(CN)_8O_6]\cdot 2H_2O$. This material always displays a more sharply defined spectrum than do the other compounds. The peaks of greatest intensity are the three in the 750–900-cm^{-1} region, and the presence of three such peaks of proper relative intensity is taken to indicate the presence of this compound as an impurity in other samples. Thus, it is concluded that the samples of $K_2[Mo(OH)_2(CN)_4]$ and $Cd[Mo(OH)_2(CN)_4]$, whose spectra are shown in Figure 3, contain $K_6[Mo^{IV}_2Mo^{VI}(CN)_8O_6]\cdot 2H_2O$ as an impurity.

Magnetic Properties.—All of the compounds prepared were found to be diamagnetic. This agrees with previous reports for tan $K_4[MoO_2(CN)_4]$[14] and blue $K_3[MoO(OH)(CN)_4]$.[11] A blue compound prepared by Bucknall and Wardlaw[6] and formulated by them as $K_3[Mo(OH)_3(H_2O)(CN)_4]\cdot 2H_2O$ has been more recently formulated as the Mo(V) compound $K_3[Mo(OH)_4(CN)_4]$ on the basis of its being paramagnetic.[18] Our blue $K_3[MoO(OH)(CN)_4]$, which is diamagnetic, would seem to be the anhydrous form of Bucknall and Wardlaw's compound. We have observed no evidence of any paramagnetic species and thus have no positive evidence for the reported compound.[18]

Ordinarily an octahedral d^2 complex would be para-

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(26) C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 3552 (1959).
(27) P. C. H. Mitchell, *J. Inorg. Nucl. Chem.*, **25**, 963 (1965).
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(29) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1951).

magnetic. In an ion of the symmetry corresponding to these *trans* complexes, the presence or absence of paramagnetism is dependent on whether the d_{xy} orbital is lower or higher than the degenerate d_{xz} and d_{yz} orbitals. The present results are consistent with the view that the d_{xy} orbital is lowest, as suggested by Lippard.[12]

Acid Ionization Constants.—Litvinchuk and Mikhalevich[30] reported measurements of hydrolysis constants at 16° for reactions of the type

$$Mo(OH)_4(CN)_4^{4-} + H_2O \rightleftharpoons Mo(OH)_3(H_2O)(CN)_4^{3-} + OH^-$$

Although we would formulate this reaction as

$$MoO_2(CN)_4^{4-} + H_2O \rightleftharpoons MoO(OH)(CN)_4^{3-} + OH^-$$

the numerical value of the constant is the same regardless of the formulation. Their values result from measurements of the pH of solutions of the appropriate salts. Although this method is satisfactory in principle, its success is dependent on using a salt quite free of the conjugate acid or conjugate base of the anion whose hydrolysis is being measured. Our experience indicates that this would be easy with $K_4[MoO_2(CN)_4$, difficult with $K_3[MoO(OH)(CN)_4]$, and very difficult with $K_2[Mo(OH)_2(CN)_4]$. The pH's they report for solutions of $K_2[Mo(OH)_2(H_2O)_2(CN)_4]$ are more basic than those we observe with $K_2[Mo(OH)_2(CN)_4]$, although these must be a single compound. Their value for the acid ionization constant of $MoO(OH)(CN)_4^{3-}$, calculated from the hydrolysis of $MoO_2(CN)_4^{4-}$, is meaningful, but the other two constants are probably not. Their value is 2.2×10^{-13} at 16°.

We have used data, like those in Figure 1, from the titration of $MoO_2(CN)_4^{4-}$ to calculate the acid ionization constants. In these calculations a value of 0.8 was used for the activity coefficients of H^+ and OH^-.

(30) V. M. Litvinchuk and K. N. Mikhalevich, *Ukr. Khim. Zh.*, **25**, 563 (1959).

The following values were obtained for acidionization constants at 25°: for $MoO(OH)(CN_4^{3-}$, $K_a = 2.4 \times 10^{-13}$; for $Mo(OH)_2(CN)_4^{2-}$, $K_a = 1.05 \times 10^{-10}$.

Visible and Ultraviolet Spectra.—Use of the ionization constants allows an estimate of the relative amounts of the various ions in a solution of fixed pH. Such values are indicated by the symbols F_{II}, F_{III}, and F_{IV} (the subscript indicates the charge of the complex) in Tables I and II for comparison with the visible and uv spectral data. The values are included to indicate in a general way the relative abundance of the three complexes; the exact numerical values cannot be correct because of changing activity coefficients in the diverse media used.

It appears that each of the three complexes has a charge-transfer absorption with a peak at 226 mμ. Solutions of acidic pH have a characteristic absorption peak at 299 mμ, but the species has not been identified.

In the visible region the absorption spectra at different pH's are similar enough so that all solutions have a color with a blue component. It appears that λ_{max} values for the individual species are approximately as follows: $MoO_2(CN)_4^{4-}$, somewhat less than 594 mμ; $MoO(OH)(CN)_4^{3-}$, about 595 mμ; $Mo(OH)_2(CN)_4^{2-}$, about 620 mμ; species present at pH <7, about 610 mμ. Apparently these absorption maxima can be shifted in the solid state, probably as a result of the varying proximity and influence of cations. For example, a KBr pellet of the red-violet compound showed a maximum at 520 mμ. The proximity of cations also affects the color *via* the effect on the high-intensity charge-transfer bands whose tails may come into the visible region. This effect is more apparent in the solids containing $Mo(OH)_2(CN)_4^{2-}$. The solid with the cation $Cd(H_2O)_6^{2+}$ is blue-purple, that with the cation K^+ is green, and that with the cation Cd^{2+} is brown-green.

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α-Molybdenum Tetrachloride. A Structural Isomer Containing Molybdenum–Molybdenum Interactions

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Molybdenum pentachloride reacts with tetrachloroethylene in carbon tetrachloride solution to give a new form of molybdenum tetrachloride which is isomorphous with the metal–metal bonded niobium tetrachloride. The magnetic properties however indicate that the molybdenum–molybdenum double bond is not completely formed, and this behavior is discussed.

Introduction

A previously reported form of molybdenum tetrachloride shows normal paramagnetic behavior for two unpaired electrons.[1] The structure consists of isolated $MoCl_6$ octahedra together with octahedra sharing edges, and the shortest molybdenum–molybdenum distance of 3.50 Å precludes the presence of significant molybdenum–molybdenum interactions.[1] This is in contrast to the tetrachlorides of the neighboring elements in the periodic table. For example the for-

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