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Reactions of the Di-μ-oxo-bis[aquaoxalatooxomolybdate(V)] Ion

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Reactions of the complex ion $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$ (I) have been investigated. On acidification with perchloric acid and hydrochloric acid, complex (I) gave molybdenum(V) aqua-dimer ion $[Mo_2O_4(H_2O)_6]^{2+}$, which was converted into the monomeric species $[MoOCl_5]^{2-}$ in concentrated hydrochloric acid. The initial reaction of complex (I) with mercaptoacetic acid, giving a complex of stoichiometry 1 ligand: 1 Mo, was followed by a slower reaction which probably gave higher complexes. In the reactions with *o*-aminophenol and 2,2'-bipyridyl, complexes of stoichiometry 1 ligand: 1 Mo and 1 ligand: 2 Mo, respectively, were formed in solutions. The following complexes have been isolated: $Mo_2O_4(dtc)_2$, $Mo_2O_3(dtc)_4$ (dtc=diethyldithiocarbamate), $MoOCl_3\cdot$phen (phen=1,10-phenanthroline), and $Mo_2O_3Cl_4(bpy)_2$ (bpy=2,2'-bipyridyl). The infrared and electronic spectra of the complexes and their probable structures are given. The relative ease of replacement of ligands from complex (I) has been discussed.

Complexes of molybdenum-(V) and -(VI) with L-cysteine,[1,2] other amino acids[3] and organic sulfur compounds[4] are of interest as models for molybdenum-containing enzymes. It has been established that most of such enzymes contain two molybdenum atoms at the active sites. Molybdenum(V) tends to produce the binuclear oxo complexes bridged with oxide ion. The property of molybdenum(V) complexes and also the variety in both the oxidation number and coordination number of molybdenum might account for the complicated conditions required in the enzymes. The presence of bridging oxygen and terminal oxygen (*i.e.* bonded to only one molybdenum) in binuclear molybdenum(V) complexes might determine the structures and reactivities of the complexes. The oxo-bridged binuclear molybdenum(V) complexes with cysteine,[1,2] dithiocarbamate,[5,6] histidine,[7] oxalate,[8] EDTA,[9] and 8-quinolinol (oxine)[10] have been studied in view of the interest in molybdenum–enzyme systems. Mitchell[11] investigated the substitution reactions of di-μ-oxo-bis-[aquaoxalatooxomolybdate(V)] ion (I), the structure of which was determined by a single-crystal X-ray diffraction study.[12] Further study on the reactions of molybdenum(V) oxalato-complex was undertaken in order to obtain a general picture of the relative ease of replacement of ligands from the binuclear complex.

Experimental

Preparations and reactions were carried out in anaerobic water under an atmosphere of nitrogen, unless otherwise stated. The solution of complex (I) was prepared from the corresponding barium salt and potassium sulfate. The barium salt $Ba[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$ was prepared according to procedures described in the literature.[8,13] Found: Mo, 29.0; C_2O_4, 26.7; Ba, 21.4%. Calcd for $BaMo_2O_{17}C_4H_{10}$: Mo, 29.1; C_2O_4, 26.7; Ba, 20.8%. The oxidation number of the molybdenum is 5.0.

Di-μ-oxo-bis[diethyldithiocarbamatooxomolybdenum(V)], $Mo_2O_4(dtc)_2$. A solution of complex (I) (1.5 mmol) in water (50 ml) was slowly added to a solution of sodium diethyldithiocarbamate (3 mmol) in water (100 ml). A yellow precipitate which formed immediately was collected by filtration, washed with water and ethanol, and dried *in vacuo* over silica gel. The complex was soluble in chloroform and 1,2-dichloroethane. Found: Mo, 35.0; C, 21.8; 5.3; H, 3.5%. Calcd for $Mo_2O_4C_{10}H_{20}N_2S_4$: Mo, 34.8; C, 21.7; N, 5.1; H, 3.6%.

μ-Oxo-bis[bis(diethyldithiocarbamato)oxomolybdenum(V)], $Mo_2O_3(dtc)_4$. A solution of complex (I) (1.25 mmol) in 0.1M-acetate buffer (50 ml, pH 3.0) was added to an ice-cold solution of diethyldithiocarbamate (10 mmol) in water (100 ml). A dark purple precipitate formed immediately and the suspension was stirred for ten minutes. The precipitate was filtered off, washed with water and ethyl ether, and dried *in vacuo* over silica gel. The complex was soluble in chloroform. Found: Mo, 23.3; C, 28.3; N, 7.0; H, 4.8%. Calcd for $Mo_2O_3C_{20}H_{40}N_4S_8$: Mo, 23.1; C, 28.8; N, 6.7; H, 4.8%.

Trichlorooxo(1,10-phenanthroline)molybdenum(V), $MoOCl_3\cdot$phen. We obtained the complex $[Mo_2O_3(C_2O_4)_2(phen)_2]\cdot 2H_2O$ according to the method of Mitchell[11] by the reaction of complex (I) with 1,10-phenanthroline in phthalate buffer solution (pH 4). The former complex (46 mmol) was refluxed in 5M-HCl (50 ml) for twenty minutes. A dark red precipitate which formed was filtered off, washed with 5M-HCl and ethanol, and dried *in vacuo* over silica gel. The complex was insoluble in water. Found: Mo, 24.5; Cl, 26.3; N, 7.4%. Calcd for $MoOCl_3C_{12}H_8N_2$: Mo, 24.1; Cl, 26.7; N, 7.0%.

μ-Oxo-bis[(2,2'-bipyridyl)dichlorooxomolybdenum (V)], $Mo_2O_3Cl_4(bpy)_2$. A phthalate buffer solution (50 ml) containing 2,2'-bipyridyl (7 mmol) and 1M-sulfuric acid (10 ml) was added to a solution of complex (I) (3.5 mmol) in phthalate buffer (50 ml, pH 4). The solution was stirred for fifteen minutes while a buff precipitate formed. The precipitate was filtered off, washed with water and ethanol, and dried *in vacuo* over silica gel. The solid was little soluble in water. The solid contained both oxalate and 2,2'-bipyridyl, whereas it contained neither potassium nor sulfate. Typical analytical values: Mo, 32.6; N, 5.1; C_2O_4, 15.6%. When the solid was refluxed in 5M-HCl, a purple black precipitate was formed. The complex was insoluble in water and common organic solvents. Found: Mo, 27.8; Cl, 19.8; N, 8.0%. Calcd for $Mo_2O_3Cl_4C_{20}H_{16}N_4$: Mo, 27.6; Cl, 20.4; N, 8.1%.

Solutions of the aqua-ion $[Mo_2O_4(H_2O)_6]^{2+}$ were obtained by the following cation-exchange separation. A solution of 2×10^{-2} M-complex (I) in 5M-perchloric acid was aquated for two days under nitrogen. The solution was adsorbed on a cation-exchange column (Dowex 50W-X2) and a yellow band was eluted from the column with 1M-perchloric acid. The analysis of the eluted solution showed that the oxidation state of molybdenum was still 5+, and the solution was free from oxalate ion. UV and visible spectra of solutions were recorded on a Hitachi 124 spectrophotometer with the use of matched silica cells and appropriate reference solutions. IR spectra of solids in potassium bromide discs were recorded on a Nihonbunko DS 301 spectrophotometer. Molybdenum was determined gravimetrically as molybdenum (VI) oxinate, $MoO_2(C_9H_6ON)_2$, after decomposition of the complexes by heating with a 1 : 1 mixture of concentrated nitric and sulfuric acids. The oxidation number of molybdenum was determined by permanganate titration of the complexes, a correction being made for oxalate. Barium was determined gravimetrically as barium sulfate and chlorine as silver chloride. Carbon, hydrogen, and nitrogen were determined by standard microanalytical procedures.

Results and Discussion

Reactions in Solution. The electronic spectrum of complex (I) varied on acidification with perchloric acid. With increasing concentration of perchloric acid, a band at 304 nm in the complex (I) spectrum shifted to shorter wavelength (about 10 nm in 5 M-perchloric acid), whereas a band at 255 nm remained unchanged.

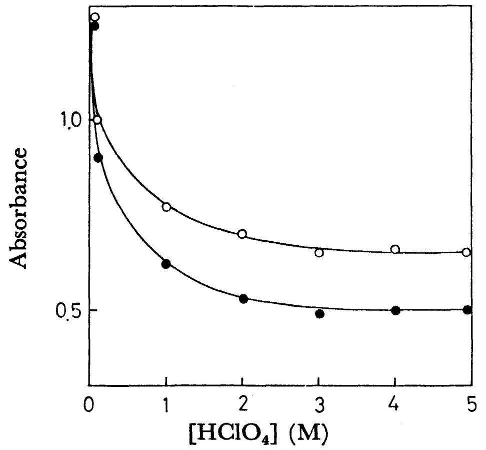


Fig. 1. The variation in absorbances of the complex (I) solution with concentration of perchloric acid. 1.5×10^{-4} M-complex (I). ○: 254 nm. ●: 304 nm.

Figure 1 shows the variation of the absorbances with the concentration of perchloric acid. We attempted to characterize the molybdenum(V) species in aqueous perchloric acid with ion-exchange method. The analytical evidence and the ion-exchange behavior indicate that the molybdenum(V) species is a +2 charged cation to which no oxalate is coordinated. It is well-known[14] that molybdenum(V) salts produce at least three species in aqueous solutions with oxo-molybdenum frameworks MoO^{3+}, $Mo_2O_3^{4+}$, and $Mo_2O_4^{2+}$, which are in an equilibrium dependent on hydrogen ion concentration. Ardon and Pernick[15] have proposed binuclear aqua-ion$[Mo_2O_4(H_2O)_6]^{2+}$ as a molybdenum(V) species in aqueous perchloric acid solutions. Sasaki and Sykes[16] conclude that the molybdenum(V) aqua-ion is stable in the concentration range of 0.5—5 M perchloric acid. Our observations are consistent with this assignment. The conclusion that we also have the molybdenum(V) aqua-dimer is supported by the measurement of the absorption characteristics. The absorption spectrum of the eluted solution has maxima at 294 nm ($\varepsilon=3400$ l mol^{-1} cm^{-1}) and 254 nm ($\varepsilon=3900$). The absorption spectrum is in good agreement with the spectra of Ardon and Pernick; 293 (3454) and 254 nm (3998),[15] and of Sasaki and Sykes; 295 (3546) and 255 nm (4320).[16] On neutralization of the molybdenum(V) aqua-dimer solution in the presence of oxalate, the peak at 294 nm shifted to longer wavelength with a significant increase in absorbance. This is probably consistent with equilibrium (1) in aqueous perchloric acid.

$$[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-} + 4H_3O^+ \rightleftharpoons [Mo_2O_4(H_2O)_6]^{2+} + 2H_2C_2O_4 \qquad (1)$$

On the other hand, a number of studies have been made of the behavior of molybdenum(V) in hydrochloric acid solutions, and monomer-dimer equilibria have been proposed.[14] The electronic spectrum of complex (I) also varied on acidification with hydrochloric acid. With an increase in concentration of hydrochloric acid, the peak at 304 nm in complex (I) initially shifted to shorter wavelength, but the direction of the shift was reversed at [HCl] = 1—2 M. Figure 2 shows the variation of absorbances with the concentration of hydrochloric acid. The absorbance at each wavelength shows a minimum at [HCl] = 1—2 M and approaches a definite value in very high concentration of hydrochloric acid. With concentrated hydrochloric acid, the solution gave the characteristic green color of the pentachlorooxomolybdate(V) ion. Details of the absorption maxima (absorption coefficient per molybdenum), 720 (20), 443 (18), 355 (560), 310 (4700), and 241 nm (5400), are in good agreement with those of $MoOCl_5^{2-}$.[17] The change in the spectrum at [HCl] < 1M might be due to the aquation of complex (I), because the spectral change is identical with that in the aquation with perchloric acid. Ardon and Pernick[15] have shown that the main molybdenum(V) species in dilute hydrochloric acid (< 1M) is the aqua-dimer $[Mo_2O_4(H_2O)_6]^{2+}$ as well as in perchloric acid. The change in spectrum of complex (I) at higher concentration of hydrochloric acid might be attributed to the conversion of the molybdenum(V)-dimer into the

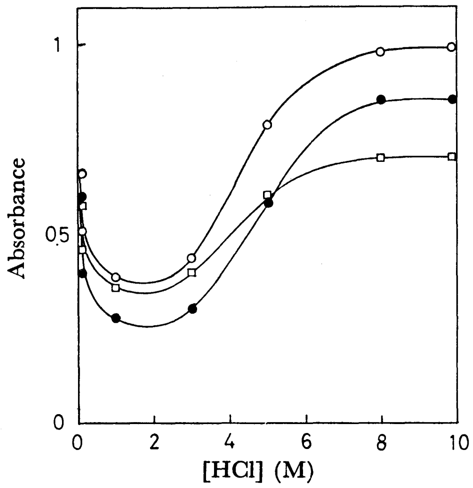


Fig. 2. The variation in absorbances of the complex (I) solution with concentration of hydrochloric acid. 10^{-4} M-complex (I). ○: 240 nm. □: 300 nm. ●: 310 nm.

monomeric species $[MoOCl_5]^{2-}$ according to the characteristic of the spectral change. When complex (I) was allowed to stand in basic solutions (pH 7—10), the band of 304 nm shifted to longer wavelength with a decrease in absorbance, whereas the band at 255 nm shifted to shorter wavelength with an increase in absorbance. The absorbance of the band at 304 nm remarkably decreased with time in higher pH, probably owing to the oxidation of molybdenum(V). Molybdenum(V) is too easily oxidizable in basic solutions to allow quantitative examination of the reaction.

Reactions of complex (I) with different ligands were carried out in aqueous solutions buffered at pH 4, in which complex (I) persists.[11] Continuous variations plots for 2,2′-bipyridyl are shown in Fig. 3. Maxima in ΔA, deviations of the absorbances of the mixed solutions from the sums of the absorbances of the components, occurred at a 2,2′-bipyridyl: complex (I) ratio of 1: 1 showing the formation of a complex of stoichiometry 1 bpy: 2 Mo. The spectrum of the mixed solution differed from that of complex (I) only in the enhanced absorbance above 350 nm and no new peaks were observed. The plot with *o*-aminophenol is shown in Fig. 4. Minimum in ΔA occurred at a ligand: complex (I) ratio of 2: 1. This corresponds to the formation of a complex of stoichiometry 1 aminophenol: 1 Mo. Molar ratio plots for mercaptoacetic acid (maa) are shown in Figs. 5 and 6. The plot at 30 minutes after mixing shows the formation of a complex of stoichiometry 1 maa: 1 Mo. The plots after 15 and 40 hours are linear up to 4 molar ratio of mercaptoacetic acid to complex (I), above which ratio both absorbances gradually approach definite values. Thus the initial reaction, giving a 1: 1 complex, is followed by a slower reaction which might give higher complexes. With the following ions and molecules there were no spectral changes, continuous variations plots being straight lines; *O*-ethyl dithiocarbonate, glycine, tartrate, malonate, thiourea, biuret, thiosemicarbazide, and phosphate.

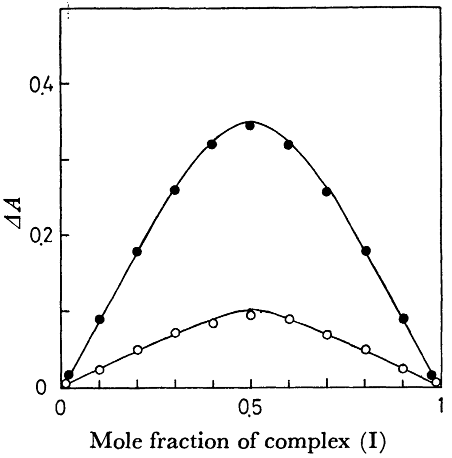


Fig. 3. Continuous variation plots for the reaction of complex (I) with 2,2′-bipyridyl.
The total concentration was 2.5×10^{-4} M. pH 4.0. ●: 400 nm. ○: 450 nm.

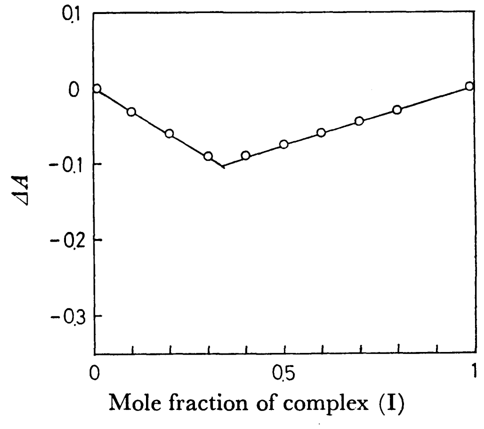


Fig. 4. The continuous variation plot for the reaction of complex (I) with *o*-aminophenol.
The total concentration was 2.5×10^{-4} M. pH 4.0, 435 nm.

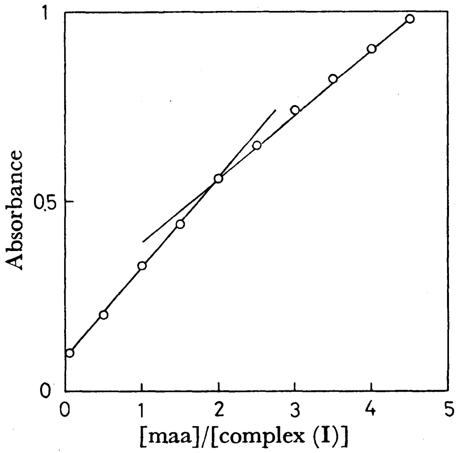


Fig. 5. The molar ratio plot at 30 min after mixing for the reaction of complex (I) with mercaptoacetic acid.
The concentration of complex (I) was 1.25×10^{-4} M. pH 4.0, 430 nm.

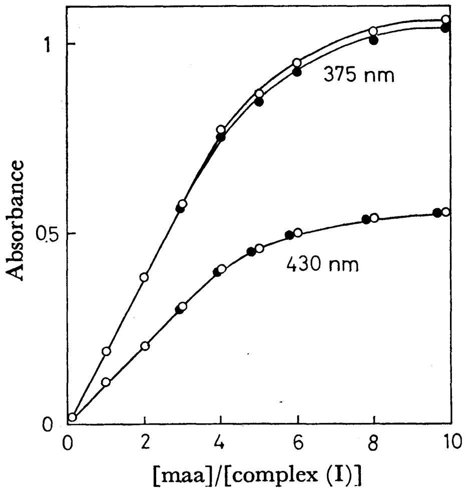


Fig. 6. Molar ratio plots at 15 and 40 hr after mixing for the reaction of complex (I) with mercaptoacetic acid. The concentration of complex (I) was 1.25×10^{-4} M. pH 4.0. ○: 40 hr. ●: 15 hr.

Complexes Isolated. The isolated complexes are listed in Tables 1 and 2. The formulas of the complexes are based on analyses and physical measurements. For complexes with dithiocarbamate, the oxidation state of molybdenum could not be determined directly because of interference by oxidizable sulfur ligands. The complexes gave the characteristic green color of the $[MoOCl_5]^{2-}$ ion in concentrated hydrochloric acid. Immediate precipitation occurs on mixing complex (I) and dithiocarbamate solutions. Initial preparation gave the products with varying molybdenum percentage and color depending upon the conditions of reaction. A higher mixing-ratio of dithiocarbamate to complex (I) at pH 4 gave smaller molybdenum percentages (dark purple color). Higher pH at a given mixing-ratio gave higher molybdenum percentages (pink color). Visible and infrared spectra suggest that the product (pink) in higher pH and lower mixing-ratio corresponds mainly to complexes of the Mo_2O_4 type, and that (dark purple) in lower pH and higher mixing-ratio to the Mo_2O_3 type. We isolated analytically pure $Mo_2O_4(dtc)_2$ and $Mo_2O_3(dtc)_4$. Our observation is consistent with Kay and Mitchell's comment[2] that molybdenum(V) complexes of the type $Mo_2O_4L_2$ are obtained from aqueous solutions under more alkaline conditions than in the preparation of the complexes $Mo_2O_3L_4$. The complex $Mo_2O_4(dtc)_2$ has recently been prepared by refluxing an aqueous solution of pentachlorooxomolybdate(V) and dithiocarbamate.[6] The complex seems to have structures closely related to the molybdenum(V) complexes with L-cysteine esters, in which unique five-coordinate structures are formed.[18] The complex $Mo_2O_3(dtc)_4$ is considered to be structurally similar to the corresponding dithiocarbonate and phosphorothiolothionate complexes, the structures of which have been determined by single-crystal X-ray crystallography.[19,20] $Mo_2O_4(dtc)_2$ could be easily converted into $Mo_2O_3(dtc)_4$ by stirring with dithiocarbamate in chloroform–methanol (4: 1) solution. Confirming Mitchell's description,[11] we obtained μ-oxo-bis[oxobis(8-quinolinolato)molybdenum(V)]hydrate from a hot solution containing complex (I) and 8-quinolinol. In the reactions of complex (I) with 8-quinolinol one bridging oxo-group of the Mo_2O_4 group was replaced giving complexes of the Mo_2O_3 group. $MoOCl_3$·phen was obtained by refluxing the complex

TABLE 1. INFRARED SPECTRA[a]

$Ba[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$							
3450s	1708vs	1675vs	1645vs	1425s	1282m	976vs	
water			oxalate			Mo=O	
955m	910m	794m	728m				
Mo=O	oxalate		MoO_2Mo				
$Mo_2O_4(dtc)_2$							
1545s, sh	1530vs	1455s	1437s	1382m	1356m	1290w	
			dtc				
1278s	1200s	1152m	1100w	1080m	1065w	972vs	956m
		dtc				Mo=O	
910m	845m	780w	734m				
	dtc		MoO_2Mo				
$Mo_2O_3(dtc)_4$							
1512vs	1490s,sh	1455s	1434s	1382m	1358m	1297w	
			dtc				
1276s	1205s	1149m	1095w	1075w	1065w	1005m	937m
			dtc				Mo=O
913s	847m	781w	750w				
	dtc		MoOMo				
$[Mo_2O_3(C_2O_4)_2(phen)_2]\cdot 2H_2O$							
3420s	3050m	1705vs	1680vs	1630s	1540m	1518m	
water	phen		oxalate		phen		
1490w	1426s	1405s	1341m	1310w	1146m	1111m	1035w
phen		oxalate			phen		
958vs	910w	876m	852s	802m	745s	725s	
Mo=O	oxalate	phen		oxalate	MoOMo	phen	
$MoOCl_3$·phen							
3030m	1625m	1601w	1575m	1516m	1489m	1426vs	
		phen					
1342m	1301w	1225m	1197w	1147m	1111m	1035w	
		phen					
963vs	874m	853vs	800m	785m	742m	725s	
Mo=O		phen			MoOMo	phen	
$Mo_2O_3Cl_4(bpy)_2$							
3040m	1660w	1598s	1560w	1490m	1468m	1440vs	
			bpy				
1315m	1280w	1242w	1171m	1157m	1075w	1044w	
			bpy				
1029m	1019m	963vs	903w	794m	777vs	753w	734m
bpy		Mo=O		bpy			MoOMo

a) All values in cm^{-1}. Abbreviations; vs: very strong, s: strong, m: medium, w: weak, sh: shoulder.

$[Mo_2O_3(C_2O_4)_2(phen)_2]\cdot 2H_2O$ in 5M-hydrochloric acid. In very prolonged refluxing, a green solution owing to $[MoOCl_5]^{2-}$ formed. The complex $MoOCl_3\cdot$phen was prepared by the reaction of the pentachlorooxomolybdate(V) with 1,10-phenanthroline in dehydrated ethanol.[21] For this complex three different isomeric forms (colored reddish-pink, pale brown, and green) are known to be interconvertible.[21] Judging from the color, our complex seems to be *cis*-isomer. A buff solid obtained by the reaction of complex (I) with 2,2′-bipyridyl at pH 4 seemed to be the Mo_2O_4 type according to the infrared spectrum. The analytical data corresponded to a Mo: oxalate: bpy ratio of 2: 1: 1. The same stoichiometry (2 Mo: 1 bpy) was also observed in the solution studies. However, no reasonable formula could be given. By refluxing the compound in 5M-hydrochloric acid we obtained the monooxo-bridged binuclear complex $Mo_2O_3Cl_4(bpy)_2$.

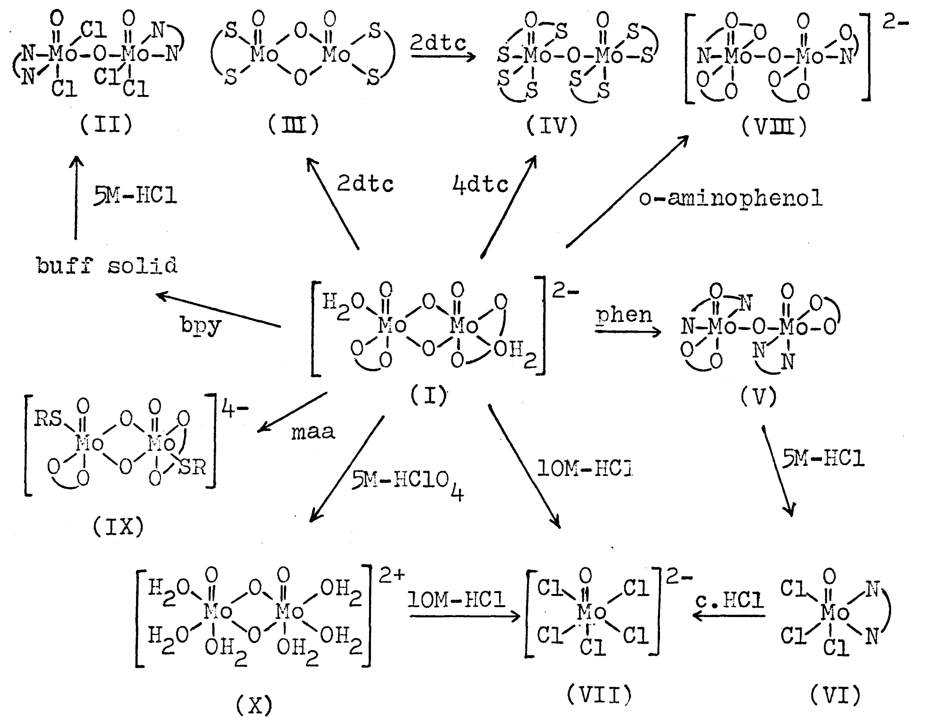
Infrared Spectra. The positions and assignments of the main bands are given in Table 1. All the complexes have a strong band at 930—980 cm^{-1} assigned to the stretching vibration of the Mo=O group. Bridge vibrations of the molybdenum-oxygen group occur at 700—800 cm^{-1}.[3,5,11] For molybdenum(V) the commonest binuclear oxo-species are the Mo_2O_3 and Mo_2O_4 groups each of which has one terminal oxygen per molybdenum and one or two bridging oxygens respectively. Wing and Callahan[22] showed that the molybdenum-oxygen stretching vibrations are a powerful tool for the characterization of the molybdenum-oxygen bridged complexes, but at present this does not seem to be always the case. Newton *et al.*[6] gave definite assignments for the infrared spectra of two series of molybdenum(V)–dithiocarbamate complexes. In the complexes with dithiocarbamate, the infrared spectra of the Mo_2O_4 groups contain two bands assigned to the terminal Mo=O vibrations and a medium band at *ca.* 740 cm^{-1} assigned to the MoO_2Mo bridge vibration. The higher (*ca.* 980 cm^{-1}) of the absorptions attributed to the terminal Mo=O vibrations is much stronger than the second band (*ca.* 960 cm^{-1}). The infrared spectra of the Mo_2O_3 groups have one band assigned to the terminal Mo=O vibration and a weak band at *ca.* 750 cm^{-1} assigned to the MoOMo bridge vibration. The split band at *ca.* 980 cm^{-1} and the medium absorption at *ca.* 740 cm^{-1} can be used as good indicators of the presence of the Mo_2O_4 moeity in complexes. These correlations are in line with those made in other complexes suggested to have the MoO_2Mo bridge.[23] Each band at about 730 cm^{-1} in complexes (I) and Mo_2O_4-$(dtc)_2$ is therefore assigned to vibrations of the MoO_2Mo groups. For complexes with 1,10-phenanthroline and 2,2′-bipyridyl, assignments of bands to the MoOMo bridge vibrations are made uncertain because of ligand vibrations at 700—800 cm^{-1}. The infrared spectra of complexes (I) and $[Mo_2O_3(C_2O_4)_2(phen)_2]\cdot 2H_2O$ have characteristic bands at *ca.* 1630—1710 cm^{-1} assigned to the C=O stretching vibration of coordinated oxalate. As noted by Jowitt and Mitchell,[5] the vibration frequency (1488 cm^{-1}) of $N{=}CS_2$ group for dithiocarbamate increases on coordination because of an increased contribution of the canonical form $Et_2N^+{=}CS_2^{2-}$. In the complex $Mo_2O_3(dtc)_4$ this vibration splits into two bands (as a shoulder) indicating that the two dithiocarbamate groups are not equivalent.[19] The presence of 1,10-phenanthroline in the complexes $[Mo_2O_3(C_2O_4)_2(phen)_2]\cdot 2H_2O$ and $MoOCl_3\cdot$phen is shown by characteristic bands at *ca.* 1625 m, 1516 m, 1426s, 1341m, 1315w, 1147m, 853s, and 725s cm^{-1}. The spectrum of the complex obtained by the reaction of complex (I) with 2,2′-bipyridyl at pH 4 has bands at 955 and 937 cm^{-1} assigned to vibrations of the terminal Mo=O group, showing that the complex probably contains the Mo_2O_4 groups.

Electronic Spectra. The positions, intensities and assignments of the absorption maxima are shown in Table 2. Complex (I) has two peaks assigned to d-d transitions in the visible region, and two intense peaks assigned to charge-transfer transitions ($O^{2-}\rightarrow Mo$) in the UV region.[8] The spectrum of $Mo_2O_3(dtc)_4$ indicated a poorly resolved shoulder at 15600 cm^{-1} assigned to a d-d transition, which is at higher energy

Table 2. Electronic spectra[a]

Compound	ν_{max} (10^3cm^{-1})	Assignments
$[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$	20.4sh(70)	d-d
in water	26.0(300)	d-d
	32.9(6700)	charge-transfer
	39.2(6600)	charge-transfer
$Mo_2O_4(dtc)_2$	31.5sh(7800)	charge-transfer
in chloroform		
$Mo_2O_3(dtc)_4$	15.6sh(600)	d-d
in chloroform	19.5(2000)	charge-transfer
	26.3(5200)	charge-transfer
	32.8sh(17700)	$\pi\rightarrow\pi^*$ of dtc
$[Mo_2O_3(C_2O_4)_2(phen)_2]\cdot 2H_2O$	28.2sh(2600)	charge-transfer
in water	36.0(38000)	$\pi\rightarrow\pi^*$ of phen
$MoOCl_3\cdot$phen	18.7(~400)	d-d
in acetone	23.8sh(~800)	charge-transfer
	27.7(2000)	charge-transfer
	32.9(11000)	$\pi\rightarrow\pi^*$ of phen

a) Molar absorption coefficients ($l\ mol^{-1}\ cm^{-1}$) are given in parentheses.



Scheme. Reaction scheme and proposed structures.
Complexes (I)—(VII) have been isolated, others being species postulated in aqueous solutions.

than the first d-d transition for the ion $[MoOCl_5]^{2-}$ ($14100\ cm^{-1}$).[17] A peak or shoulder at less than $18000\ cm^{-1}$ is observed for molybdenum(V) complexes, $Mo_2O_3L_4$ (L=dithiocarbamate, dithiocarbonate, or phosphorothiolothionate), and is assigned to a d-d transition.[5] Strong peaks at 18000—$29000\ cm^{-1}$ are characteristic of oxo molybdenum(V) complexes with polarizable ligands,[5] and cover peaks due to d-d transitions expected in this region. In agreement with Jowitt and Mitchell,[5,11] we assigned the peaks in this region in complexes $Mo_2O_3(dtc)_4$ and $[Mo_2O_3(C_2O_4)_2(phen)_2]\cdot 2H_2O$ to ligand-to-molybdenum charge-transfer transitions. The spectrum of $Mo_2O_4(dtc)_2$ was essentially featureless except for a poorly resolved shoulder at $31500\ cm^{-1}$. We assigned the peak to a charge-transfer transition because of its high absorption coefficient. $MoOCl_3\cdot$phen has only one peak below $20000\ cm^{-1}$. For the complex $MoOCl_3\cdot$phen (reddish-pink), Saha and Halder[21] observed two peaks at 13700 ($\varepsilon=179$) and $18900\ cm^{-1}$ ($\varepsilon=282$) assigned to d-d transitions. The complex anion $[MoOCl_5]^{2-}$ has also two peaks at 14100 (20) and $22500\ cm^{-1}$ (18) assigned to d-d transitions.[17] The complex $MoOCl_3\cdot$phen we prepared was too insoluble into common organic solvents to observe weak peaks of ε less than 200. Both peaks at 23800 and $27700\ cm^{-1}$ in the complex are assigned to charge-transfer transitions according to the values of the absorption coefficient. A strong peak at $32900\ cm^{-1}$ is assigned to the internal transition ($\pi\rightarrow\pi^*$) of coordinated 1,10-phenanthroline, which is at lower frequency than that of free 1,10-phenanthroline. Peaks at wave numbers greater than $32000\ cm^{-1}$ are assigned to $\pi\rightarrow\pi^*$ transitions of the ligands except for complex (I).

Conclusion

Reactions involved in this paper are summarized in the Scheme. In the initial reaction with mercaptoacetic acid, a complex of stoichiometry 1 ligand: 1 Mo was formed in solution. Similarity of the spectrum of the mixed solution to that of complex (I) except for the enhancement of absorption above 360 nm suggests that no significant structural change occurs in the reaction. We assume that two coordinated waters are replaced by mercaptoacetic acid. With *o*-aminophenol a complex of stoichiometry 1 ligand: 1 Mo was formed in solution. Because of a strong absorption maximum of *o*-aminophenol at 435 nm, we cannot observe the remarkable characteristics in spectrum of the complex. The electrical migration studies showed that the complex was an anion. It is reasonable to assume that coordinated waters and one bridging oxygen were replaced by *o*-aminophenol, because the replacement of oxalate should produce a nonelectrolyte. As the substitution reactions of complex (I), there are four possible stages involving replacement of coordinated water, bridging oxygen, oxalate, and terminal oxygen, respectively. Mitchell[11] discussed the relative ease of replacement of ligands from complex (I) and showed that, qualitatively, the order of the ease was $H_2O>$one bridging oxygen$>$oxalate$\gg$terminal oxygen. We agree with Mitchell in concluding that the replacement of coordinated water is easiest. In reactions of complex (I) with 1,10-phenanthroline and *o*-aminophenol, the cleavage of one oxygen bridge of the Mo_2O_4 group occurred keeping oxalate. On the other hand, in the formation of $Mo_2O_4(dtc)_2$ and of $[Mo_2O_4(H_2O)_6]^{2+}$ the replacement of oxalate occurred without any cleavage of oxygen bridge. The relative ease of replacement of one bridging oxygen and oxalate probably varies with nucleophiles in disagreement with Mitchell's conclusion.[11] Molybdenum(V) has a particular affinity for dithiocarbamate as well as 8-quinolinol. Nevertheless neither ligand can cleave all oxygen bridges of the Mo_2O_4 group and both ultimately give the single-bridged $Mo_2O_3L_4$ species. Strongly acidic conditions are required for the formation of a mononuclear species. Replacement of terminal oxygen whose bond order to molybdenum is approximately two[24] is very unlikely to occur in aqueous solutions (even in concentrated hydrochloric acid). Special stability of monooxo molybdenum(V) moiety MoO^{3+} in aqueous solutions has led to certain interesting investigations of the chemistry of the oxo molybdenum(V) ions.[21,25]

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