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Acetylacetonate Complexes of Molybdenum(V) and Molybdenum(VI). I.

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The compound $MoO_2(C_5H_7O_2)_2$ has been reinvestigated and those methods of synthesis yielding reddish-yellow products have been found to be mixtures of $MoO_2(C_5H_7O_2)_2$ and $Mo_2O_3(C_5H_7O_2)_4$. Identification of mixtures was made by comparison of the visible spectrum and X-ray diffraction patterns with samples of known purity. The various syntheses for $Mo_2O_3(C_5H_7O_2)_4$ and $MoO_2(C_5H_7O_2)_2$ have been evaluated. A new method of synthesis of $Mo_2O_3(C_5H_7O_2)_4$ is reported. The ultraviolet and visible spectra of $Mo_2O_3(C_5H_7O_2)_4$ and $MoO_2(C_5H_7O_2)_2$ have been obtained in a variety of solvents and the electronic transitions assigned. The infrared spectrum and the mode of formation of $Mo_2O_3(C_5H_7O_2)_4$ is discussed. Several additional molybdenum acetylacetonate complexes reported to contain molybdenum(V) and (IV) have been reinvestigated.

Introduction

During a study of molybdenyl compounds, it became necessary to prepare $MoO_2(acac)_2$, where acac = acetylacetonate ion. This compound was first prepared by Gach,[1] but incorrectly formulated as $Mo(acac)_2$. Rosenheim and Bertheim[2] later formulated the compound as $MoO_2(acac)_2$. Morgan and Castell[3] confirmed the latter formula and proved the product to be the same as that prepared by Gach.[1] Additional methods of preparation have been cited in the literature,[4-9] but the color and melting point of the products vary considerably. During the course of this study, Bernal[10] reported the free radical and autoxidation-reduction of $MoO_2(acac)_2$ under varying conditions to $Mo_2O_3(acac)_4$. Because of certain discrepancies with the work of Bernal[10] and the fact that our studies are more extensive, we wish to report the findings. To clear up certain questions concerning the nature of other acetylacetonates reported to contain molybdenum(V) and (IV), the investigation includes these complexes.[11-13]

Experimental Section

Reagents. Acetylacetone, Aldrich puriss grade, was used without further purification. All molybdenum compounds were gifts of Climax Molybdenum Corp. and used as received. All solvents were used as received except those required for ultraviolet and visible spctra . These were purified using standard procedures.[14]

Analyses. Carbon and hydrogen analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn., or by the departmental analyst. Molybdenum content was determined by the method of Tyree.[15]

Measurements. Infrared spectra were obtained as KBr disks or as nujol mulls on a Perkin-Elmer 521 spectrophotometer. The sodium chloride region was calibrated with polystyrene, and water vapor served as the calibration substance for the low frequency region.[16] The accuracy is $\pm 2\ cm^{-1}$. Visible and ultraviolet spectra were obtained with a Beckman DK-2A recording spectrophotometer. X-ray diffraction patterns were obtained using a Picker biplane Defractometer and Cu K α radiation with a nickel filter. Molecular weights were determined with a Mechrolab Model 301 Vapor Pressure Osmometer. Differential thermoanalysis was obtained using a Fisher Model 260 Differential Thermolyzer.

Dioxobis(acetylacetonato)molybdenum(VI), $MoO_2(acac)_2$. A modified procedure of Jones[7] was found to yield the purest product in the highest yield. Sodium molybdate dihydrate 4.85 g (2.04 mmoles) is dissolved in 50 ml of water and 6 N hydrochloric acid is added until the pH = 1. Then 6 ml of acetylacetone (6.0 mmoles) is added to the solution with vigorous stirring that breaks up globules which contain entrapped acetylacetone. The yellow solid, 5.88 g, (90% yield) is isolated by filtration, washed

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with 2 parts cold (0°C) ethanol, 2 parts acetone and dried.

If the filtrate is allowed to stand 4-5 days, another 6% of $MoO_2(acac)_2$ can be isolated. The product can be recrystallized from (1:20) acetylacetone: ethanol mixture with a minimum of heat. *Anal.* Calcd. for $C_{10}H_{14}O_6Mo$: C, 36.82; H, 4.32; Mo, 29.41. Found: C, 36.74; H, 4.36; Mo, 29.52. Molecular weight determination in ethanol gave values of 331, 340 and 325 (Calcd. 328).

$MoO_2(acac)_2$ will slowly turn blue when exposed to sunlight. It is very stable if washed free of acetylacetone and dried thoroughly. If all the acetylacetone is not removed, the product slowly becomes tinged with red.

μ-oxo-dioxotetrakis-(acetylacetonato)-dimolybdenum-(V), $Mo_2O_3(acac)_4$. Into a pyrex tube, 2 cm in diameter and 15 cm long, are placed 30 ml of acetylacetone and 3.0 grams of $MoO_2(acac)_2$. The tube is sealed and heated at 210°C for 24 hours. After the tube is cooled and opened, 2.18 g (80%) of $Mo_2O_3(acac)_4$ is isolated by filtration, washed with ethanol, then acetone and dried. By concentration of the mother liquor, an additional 0.55 g (11%) can be obtained. *Anal.* Calcd. for $C_{20}H_{28}O_{11}Mo_2$: C, 37.57; H, 4.43; Mo, 30.16. Found: C, 37.92; H, 4.31; Mo, 30.32.

Molecular weight determination is impossible because of the limited solubility of $Mo_2O_3(acac)_4$ in suitable solvents. The product is very stable in air.

Mixture Separation. Reddish-orange $MoO_2(acac)_2$ prepared by the method of Fernelius, *et al.*,[4] is extracted with dry hexane for one week. The total yield of $Mo_2O_3(acac)_4$ remaining in the thimble is less than 5%. Purity of the $Mo_2O_3(acac)_4$ is determined by elemental analysis and comparision of the X-ray diffraction pattern, visible and infrared spectra with an authentic sample. Isolation of the $MoO_2(acac)_2$ is not possible due to decomposition resulting from the length of time the sample is heated.

Results and Discussion

Evaluation of the Syntheses. Since numerous methods appear in the literature for the preparation of $Mo_2O_3(acac)_4$ and $MoO_2(acac)_2$, all the procedures have been reproduced and evaluated on the basis of purity, percent yield and availability of starting materials. For $MoO_2(acac)_2$, a modification of the method of Jones[7] was found to be the best. The use of hydrochloric acid in place of nitric acid is preferable because of the increased solubility of the resultant molybdenum species. The use of MoO_3 is not satisfactory due to the large quantity of NH_4OH required. In the method of Morgan and Castell,[3] the yield is low and the product is contaminated with molybdenum blue. A modified Larson and Moore[6] preparation is good, but requires MoO_2Cl_2 as the starting material. The method of Fernelius, *et al.*,[4] is unacceptable for the product is contaminated with $Mo_2O_3(acac)_4$.

The preparation of $Mo_2O_3(acac)_4$, from a neutralized hydrochloric acid solution of MoO_3 which had been reduced with Mo, was thought to be a good method,[17] as the spectra and analysis were good, but the X-ray diffraction pattern showed the presence of molybdenum metal. Oxidation of $Mo(acac)_3$ [18] is not feasible since the starting material is difficult to obtain and the purification of the oxidation product is tedious. A complex reported to be $MoO_2(acacH)_2$,[13] formed by the reduction of $MoO_2(acac)_2$ with zinc, was found to be $Mo_2O_3(acac)_4$, but the method is poor since $Zn(acac)_2$ is a contaminant. Hydrolysis of $MoOCl(acac)_2$,[6] is a good method, but it requires $MoOCl_3$. The sealed tube reaction of $MoO_2(acac)_2$ and acetylacetone provides a simple almost quantitative conversion to $Mo_2O_3(acac)_4$.

Identification of the Mixture by Spectrographic Means. In the metal-oxygen stretch frequency region between 900-1000 cm^{-1}, $MoO_2(acac)_2$ absorbs at 938 and 910 cm^{-1}, while $Mo_2O_3(acac)_4$ absorbs at 958 and 930 cm^{-1}. Failure of previous workers[4,6,19,20] to recognize the $Mo_2O_3(acac)_4$ impurity is due to the fact that 7-10% is necessary for appearance of the 958 cm^{-1} absorption band and under normal reaction conditions,[4] the percentage formed is less than half this value. Bernal[10] has indicated that the reaction of $MoO_2(acac)_2$ or MoO_3 under the reflux with acetylacetone (8 hours former, 18 hours latter) yields $Mo_2O_3(acac)_4$ based on X-ray diffraction data. This does not agree with the present study as indicated by the amount of $Mo_2O_3(acac)_4$ isolated by extraction, the infrared or visible spectra or the X-ray diffraction pattern intensities. Our X-ray data, given in Table I, indicates that the predominate species is still $MoO_2(acac)_2$.

Since the visible region is more sensitive to small amounts of impurities, it is possible to observe the 490 mμ band attributable to $Mo_2O_3(acac)_4$ in 0.5% concentration. Thus the visible spectra obtained by Bartecki[19,20] for $MoO_2(acac)_2$ indicates contamination with $Mo_2O_3(acac)_4$.

Formation of $Mo_2O_3(acac)_4$. From the literature and the observations presented earlier in this paper, three possibilities for the contamination of $MoO_2(acac)_2$ exist. Acetylacetone can act as a reducing agent as illustrated by the formation of $VO(acac)_2$ from V_2O_5 and acetylacetone,[21] but in the reaction with MoO_3, complex formation takes precedent over reduction since the primary product is $MoO_2(acac)_2$. The possibility of a photochemical reaction involving acetylacetone and/or $MoO_2(acac)_2$ has been observed by Bernal[10] and by the current work. The importance of temperature is evident from a comparison of the preparation of $MoO_2(acac)_2$ from MoO_3 and acetylacetone in ethanol and from MoO_3 and acetylacetone. The former yields no $Mo_2O_3(acac)_4$, while the latter yields up to five percent. Additional proof can be

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Table I. X-ray powder diffraction data

$Mo_2O_3(acac)_4$		Mixture		$MoO_2(acac)_2$	
d	I[a]	d	I[a]	d	I[a]
8.19	s	8.19	w		
7.82	vs	7.82	mw		
7.40	ms	7.37	w		
7.23	ms	7.23	w		
6.93	w				
		6.91	w	6.91	m
		6.55	mw	6.55	ms
6.51	m	6.51	m		
		6.23	s	6.23	s
		6.15	vs	6.15	vs
5.96	m				
		5.79	mw	5.79	m
		5.59	m	5.59	m
5.19	m	5.18	w		
		5.06	w	5.06	w
				5.04	w
4.98	w				
4.84	w				
				4.80	w
4.13	w				
				4.11	w
4.07	m	4.07	w		
				3.97	w
3.93	mw				
		3.90	m	3.90	m
3.88	m				
		3.83	w	3.83	w
3.75	m				
				3.69	w
3.56	w				
		3.50	m	3.50	m
3.49	m				
		3.39	w	3.40	w
		3.32	w	3.32	w
		3.21	w	3.21	w
		2.66	w	2.67	w
		2.61	w	2.61	w

[a] visual estimation

obtained from the synthesis of $Mo_2O_3(acac)_4$ in a sealed tube, since too low a temperature results in decreased conversion of $MoO_2(acac)_2$ to $Mo_2O_3(acac)_4$.

While temperature is important, sufficient acetylacetone must be present for the formation of $Mo_2O_3(acac)_4$. To illustrate, Bernal[10] has shown that $MoO_2(acac)_2$ when heated at 100°C for two hours yields a green solid containing Mo(V). Fernelius *et al.*,[4] state that boiling $MoO_2(acac)_2$ in benzene yields a yellow-green solid of undetermined composition. Archer[22] points out that $MoO_2(acac)_2$ decomposes at room temperature turning green eventually, but the infrared does not indicate the formation of new complexes. We have followed the decomposition by thermal gravimetric methods in the hope of isolating the complex $MoO_2(acac)$, but there was only a gradual weight loss with the increase in temperature.

Taking these factors into account it is possible to suggest a mechanism for the formation of $Mo_2O_3(acac)_4$ based on the work of Arnett and Mendelsohn.[23] They have suggested in the destructive autoxidation of $Fe(acac)_3$, the formation of a free radical with the concomitant reduction of unity in the oxidation state of the iron. Bernal,[10] on the basis of ESR, indicates the formation of MoO^{3+} when $MoO_2(acac)_2$ is heated. Dimerization following the reaction scheme, $2MoO^{3+} + H_2O \rightleftarrows [MoO{-}O{-}MoO]^{4+} + 2H^+$, and subsequent reaction with acetylacetone would yield $Mo_2O_3(acac)_4$. MoO^{3+} and H_2O could be formed by the complex organic radicals produced by the destructive autoxidation of $MoO_2(acac)_2$.

Larson and Moore[6] report the formation of red-orange $MoO_2(acac)_2$ from the reaction of MoO_2Cl_2 and acetylacetone, followed by the addition of water. We have found that the addition of MoO_2Cl_2, to a solution of acetylacetone in water, does not result in the formation of $Mo_2O_3(acac)_4$. This situation is more difficult to explain. One possibility is the reaction of acetylacetone and water to form a complex species which does not have reducing properties. Second, the reaction of MoO_2Cl_2 and acetylacetone may be incomplete and the addition of water results in the formation of $MoO(OH)_2Cl_2$ which reacts with acetylacetone in the presence of HCl to form the Mo—O—Mo linkage.

Infrared Spectra. Experimental and theoretical investigations on the systems $M(acac)_2$ and $M(acac)_3$ have contributed to our understanding of the spectra of metal acetylacetonates.[24-30] Substantial agreement exists in the region above 700 cm^{-1} which contains the modes primarily derived from the ligand. Disagreement still exists in those areas below 700 cm^{-1} involving metal-oxygen modes and these modes coupled with $C{-}CH_3$ bend or ring deformations.

A frequency assignment for $MoO_2(acac)_2$ has recently been published[31] based on the interpretation of $Cr(acac)_3$.[24] There is no evidence in the spectrum of contamination with $Mo_2O_3(acac)_4$ and we are in complete agreement with the position of the bands. The spectra of $MoO_2(acac)_2$, $Mo_2O_3(acac)_4$ and $MoOCl(acac)_2$ below 700 cm^{-1} are far more complex than $Cr(acac)_3$. The complexity is probably due to gross structural differences and without additional information, such as the use of ^{18}O labeled acetylacetone, frequency assignments based on a simple $M(acac)_3$ model must be regarded as tentative.

As a detailed study of the infrared spectrum of $Mo_2O_3(acac)_4$ has not been made, the frequencies and tentative assignments are given in Table II. The different types of molybdenum-oxygen frequencies have been discussed previously.[8,32] No metal sensitive bands could be found below 400 cm^{-1}, as observed by Mikami, *et al.*,[25] for other metal acetylacetonates.

Ultraviolet and Visible Spectra. The spectra have been recorded in a series of solvents to determine the identity of the transitions and their effect on possible decomposition of the complexes. The results are given in Table III. The position of the maxima are in good agreement with those previously repor-

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Table II. Vibrational Frequencies (cm^{-1}) For $Mo_2O_3(acac)_4$ [a]

Frequency	Predominant mode
2980 vw (sh) [b]	C—H stretch
2940 w (sh)	CH_3 deg. stretch (in-plane)
2915 w	CH_3 sym. stretch
2840 w (sh)	CH_3 deg. stretch (out-of-plane)
1580 vs (sh)	(C=O) symm. stretch
1560 vs	(C=O) symm. stretch
1510 vs	(C=O) asymm. stretch
1422 m	CH_3 deg. def.
1355 vs (br)	(C=O) asymm. stretch + CH_3 sym. def.
1272 s	C—CH_3 stretch + C=C sym. stretch
1188 w	C—H def. (in-plane)
1027 m	CH_3 deg. rock
1010 m (sh)	CH_3 deg. rock
958 s	Mo = O asymm. stretch
949 m (sh)	Mo = O asymm. stretch
930 m	C—CH_3 stretch + C=O stretch
806 m	C—H def. (out-of-plane)
778 m	Mo—O—Mo asymm. stretch (?)
678 m	Ring def. + Mo—O stretch
660 mw	Ring def. + C—CH_3 (stretch) + C—CH_3 (in-plane bend)
650 w	C—H out-of-plane bend
608 mw	C=C=C (out of plane bend)
572 m	out-of-plane ring def.
548 m	out-of-plane ring def.
460 ms	Mo—O stretch
	Mo—O stretch
435 m	Mo—O—Mo symm. stretch (?)
410 m	In-plane ring def.
383 w	C—CH_3 def.
350 w (br)	?

[a] nujol mull or KBr pellet; [b] vw = very weak, w = weak, sh = shoulder. m = medium, s = strong, vs = very strong, br = broad,

Table III. Visible and Ultraviolet Spectral Data for $Mo_2O_3(acac)_4$ and $MoO_2(acac)_2$

		$MoO_2(acac)_2$		$Mo_2O_3(acac)_4$	
Solvent		λ_{max} mμ	ε_0(l. mole^{-1} cm^{-1})	λ_{max} mμ	ε_0(l. mole^{-1} cm^{-1})
CH_3CN		317	5,110	750	361
		263	11,165	487	9,250
		208	12,963	405	3,000
				327	15,234
				248	21,900
$C_5H_8O_2$		343	4,845	492	7,624
				396	2,893
				346	10,362
C_6H_6		317	4,754	490	9,435
		282	18,531	408	3,862
				328	14,983
				278	22,480
$CHCl_3$		317	6,577	488	9,232
		273	23,960	320	14,047
				272	22,000
CH_2Cl_2		315	6,595	750	457
		272	20,229	488	10,550
				412	4,220
				328	15,530
				250	23,549
$C_4H_4O_2$		320	6,472	Decomposes	
		272	19,981		
C_2H_5OH	100%	317	6,854		
		272	27,435		
	95%	317	7,058	320	16,240
		273	23,363	270	22,116
	90%	273	12,210		
	67%	273	11,362		

ted, but in several cases differences in the extinction coefficients have been observed. The complexes have a solvent dependent maximum, 263-282 mμ ($\varepsilon_o \cong 20{,}000$), which can be assigned to the $\pi \rightarrow \pi^*$ transition[33] with the typical increase in extinction coefficient.[34] Greater deviation in the position of the peak was observed for $Mo_2O_3(acac)_4$. No correlation between the position or intensity of the maximum and the polarity of the solvent was found. Decomposition with time or increase in water concentration of ethanol was observed with $MoO_2(acac)_2$, as there is a decrease in the intensity of the $\pi \rightarrow \pi^*$ transition with a concomitant shift of the band towards that of free acetylacetone.

The shoulder at 317 mμ in $MoO_2(acac)_2$ is probably not the $n \rightarrow \pi^*$ transition, since the intensity is too great and the band is insensitive to the polarity of the solvent. Partial shielding of the ring oxygens by neighboring CH_3 groups sometimes diminishes solvent effects,[33] so the $n \rightarrow \pi^*$ transition cannot positively be ruled out. Moore and Rice[8] propose the $\pi \rightarrow \pi^*$ transition possibly coupled with some ligand oxygen-metal $d\pi$–$p\pi$ character at 314 mμ. However, the unassigned band at 262 mμ is more consistent with the $\pi \rightarrow \pi^*$ transition and the 314 mμ band to the transfer of an electron from the molybdenyl group to an empty molybdenum orbital. In $Mo_2O_3(acac)_4$, the shoulder at 320-330 mμ may be the ${}^2B_2 \rightarrow {}^2E(II)$ transition with the increased intensity probably attributed to coupling with the Mo—O—Mo bridge.

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The visible spectrum of $Mo_2O_3(acac)_4$ consists of peaks at 750 ($^2B_2 \rightarrow {}^1B_1$), [acac→Mo(V)] and 405 mμ ($^2B_2 \rightarrow {}^2B_1$). Larson and Moore[32] did not observe the 750 mμ absorption possibly due to a low concentration of $Mo_2O_3(acac)_4$. Bartecki and Dembicka[19] have reported that the spectrum of $MoO_2(acac)_2$ in acetylacetone contains bands at 768, 492 and 344 mμ. The first two bands are due to $Mo_2O_3(acac)_4$ impurity.

Other Molybdenum(V) and (VI) Acetylacetonate Complexes. Gredenic and Korpar-Colig[13] have reported that $MoO_2(acac)_2$ in hot acetylacetone is reduced by zinc to a brown complex which they formulated as $MoO_2(acacH)_2$. It was believed to contain neutral acetylacetone because of the absence of the 1188 cm^{-1} and 728 cm^{-1} bands attributed to the C–H frequency. Fackler[35] has questioned this formulation, while Bernal[10] indicates the reaction yields $Mo_2O_3(acac)_4$. We have prepared the product according to the procedure of Grdenic and Korpar-Colig[13] and identified the product as a mixture of $Zn(acac)_2$ and $Mo_2O_3(acac)_4$. The product does not contain neutral acetylacetone, as no absorption occurs above 1600 cm^{-1}. In addition, the 1188 cm^{-1} band, which appears as a strong band in $MoO_2(acac)_2$, is very weak in $Mo_2O_3(acac)_4$ and is frequently undetected in the infrared.

Further interest was shown in the molybdenum(V) complex formulated as $Mo(OH)_3(acac)_2 . 3H_2O$[11,12] or $MoO(OH)(acac)_2 . 4H_2O$[36] since there is the possibility the complex is dimeric. All attempts to prepare the complex resulted in the formation of $Mo_2O_3(acac)_4$ and $MoO(OH)_3$. Colton and Rose[37] have proposed that a hydrochloric acid solution of Mo^V exists as:

$$\begin{array}{ccccc} MoOCl_5^{2-} & \rightleftarrows & [Mo_2O_2(OH)_2Cl_8]^{4-} & \rightleftarrows & [Mo_2O_3Cl_8]^{4-} \\ >8\,M\ \mathrm{HCl} & & 5\text{-}6\,M\ \mathrm{HCl} & & 1\text{-}3\,M\ \mathrm{HCl} \\ \mathbf{1} & & \mathbf{2} & & \mathbf{3} \end{array}$$

This suggests that $Mo_2O_2(OH)_2(acac)_4$ can be prepared under the right conditions, since we have been able to prepare $Mo_2O_3(acac)_4$ by the substitution of four acetylacetonate groups for the eight chloride ions in 3. However, we feel that the formation of 2 is more pH dependent than suggested by Colton and Rose[37] and that very exacting conditions are necessary for the formation of $[Mo_2O_2(OH)_2Cl_8]^{4-}$.

Recently, Afanasev, Bantysh and Knyazev[9] reported the existence of the same species $MoO(OH)(acac)_2$ by the extraction of an acidic, aqueous solution of Mo^V with chloroform. Insufficient analytical data and physical measurements are given to substantiate their formulation. We have been unable to isolate a compound with the limited experimental procedure given.

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