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Mass Spectra and Structural Factors in the Air Stability of Carboxylate Complexes of Mo_2^{4+}

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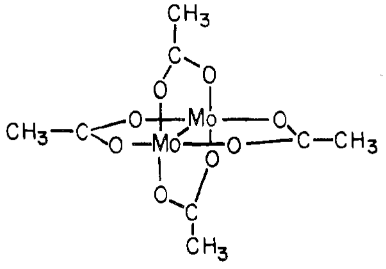
The syntheses of some new tetra-μ-carboxylato-dimolybdenum(II) complexes are reported. A wide range of air stabilities is observed. It is demonstrated that structural factors which impede binding coaxial to the metal-metal bond lead to air stability. Other factors are also shown to be important. The mass spectra of several of the compounds are reported and interpreted. The principal fragments are those consistent with important valence states of each molybdenum in the binuclear unit being 2+, 2.5+, and 3+.

Introduction

During the last 10 years it has been demonstrated that many complexes of the binuclear metal ion Mo_2^{4+} may be prepared. The first such compounds were the tetra-μ-carboxylato-dimolybdenum(II) species typified by tetra-μ-acetato-dimolybdenum(II), I.[1,2] Subsequent preparation of $Mo_2Cl_8^{4-}$ from I provided evidence that the Mo_2^{4+} unit could survive substitution reactions. Its structure indicated the existence of a quadruple metal-metal bond between the two molybdenum ions.[3] Such a bond is remarkable not only because of its high order but also because it may be the strongest bond in chemistry.[4]



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Paradoxically, these compounds are often quite air sensitive despite the postulated great bond strength. The rationalization for this is that the binuclear ion sacrifices one very strong bond to make many rather strong bonds when it forms higher valent oxides. Considerable variation in air sensitivity is reported for the molybdenum carboxylates heretofore studied. For example, the *p*-tolylcarboxylate is extremely air sensitive while the benzoate is rather stable.[5] As part of a project to investigate the properties of Mo_2^{4+} compounds, we have been studying the means by which this ion may be stabilized. Herein we report the preparation of a number of new carboxylate complexes of this ion some of which by virtue of steric factors are quite stable to air oxidation. We also report the mass spectra of some of these compounds.

Fragmentation patterns of coordination compounds have been rationalized to the ground-state chemistry of the metal ion. As pointed out by Shannon and Swan[6] and verified by others,[7-12] the major fragments of coordination compounds are often those which have the metal ion in its most important oxidation states. This rule is evidently a reflection of the relative thermodynamic stability of common valence states. The mass spectral fragmentation patterns of the molybdenum carboxylates may be interpreted by means of this rule.

Experimental Section

Materials. Tetra-μ-carboxylato-dimolybdenum(II) compounds were generally prepared by refluxing the carboxylic acid with hexacarbonylmolybdenum(0). Conditions were essentially those published for several representative arylcarboxylates.[5] Table I summarizes procedures used for each compound and analytical data obtained. Except where noted reflux times were 3–4 hr and 25 ml of diglyme was used as the solvent. Drying with $CaCl_2$ and subsequent distillation proved to be sufficient purification for the diglyme. It should also be pointed out that the color of aromatic dimolybdenum(II) carboxylates depends on the particle size. Large particles are usually red, but when they are ground up to a fine powder, the color becomes bright yellow. The acetate and propionate complexes were prepared by the method of Stephenson, *et al.*,[1] and the formate complex was prepared from the trifluoromethanesulfonate complex.[13]

Measurements. Mass spectra were obtained with a Varian cycloidal instrument. Ionization was achieved by bombardment with 60-eV electrons. Samples were sublimed into the ionization chamber at 150–200°. Spectra were calibrated by addition of perfluoroalkanes.

Results and Discussion

Intrigued by the great difference in air sensitivity for the tetra-μ-benzoato-dimolybdenum(II) and tetra-μ-*p*-toluencarboxylato-dimolybdenum(II) mentioned in the Introduction, we elected to synthesize a number of substituted molybdenum arylcarboxylates and study their rates of oxidation. As the compounds were being prepared, it became apparent that in the usual methods the compounds are nearly insoluble in solvents other than those with which they react. Therefore we were forced to select the straightforward though crude method of simply observing samples exposed to laboratory air and recording the time required for them to be entirely discolored. To do this, samples were ground to fine powders and placed on watch glasses. Results of this study are recorded in Table II. Despite all the obvious disadvantages of this approach, differences of air sensitivity are sufficiently great that an important steric factor in the oxidation is clearly revealed.

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Table I. Synthetic and Analytical Data for the Tetra-μ-carboxylato-dimolybdenum(II) Complexes

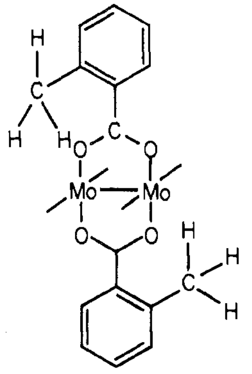
Amt, g			% calcd		% obsd	
Ligand	$Mo(CO)_6$	Compd	C	H	C	H
1.85	1.4	(o-methylbenzoate)$_4$Mo$_2$	52.4	3.8	52.63	4.06
1.0	0.85	(1-naphthoate)$_4$Mo$_2$[a]	60.3	3.2	60.41	3.26
0.97	0.80	(2-naphthoate)$_4$Mo$_2$	60.3	3.2	60.83	3.75
1.02	0.81	(p-chlorobenzoate)$_4$Mo$_2$	41.3	1.92	42.48	2.55
2.2	2.0	(o-chlorobenzoate)$_4$Mo$_2$[b]	41.3	1.92	41.38	1.80
0.49	0.36	(anthracene-9-carboxylate)$_4$Mo$_2$	66.8	3.3	66.80	3.03
1.05	0.80	(thiophene-2-carboxylate)$_4$Mo$_2$	34.28	1.71	34.43	2.08
0.26	0.20	(furan-2-carboxylate)$_4$Mo$_2$	37.7	1.9	37.52	1.99
2.7	1.6	(p-fluorobenzoate)$_4$Mo$_2$[c,d]				

[a] After refluxing, half the solvent was distilled off. The product crystallized upon standing overnight in a refrigerator. [b] Refluxed 3 hr in 10 ml of diglyme; crystallizes overnight at 0°. This compound is quite soluble in ethanol and ether. [c] The solution was refluxed for 6 hr. Half the solvent was distilled off. Orange crystals separated overnight in a refrigerator. The product is rather soluble in ethanol. [d] Elemental analyses varied; however, an intense molecular ion was observed in the mass spectrum.

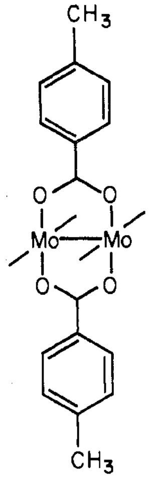
Table II. Relative Air Stability of Some Tetra-μ-carboxylato-dimolybdenum(II) Complexes

Compd	Time required for loss of color
(o-methylbenzoate)$_4$Mo$_2$	5 days
(p-methylbenzoate)$_4$Mo$_2$	10 hr
(1-naphthoate)$_4$Mo$_2$	1 year
(2-naphthoate)$_4$Mo$_2$	2 days
(p-chlorobenzoate)$_4$Mo$_2$	12 hr
(o-chlorobenzoate)$_4$Mo$_2$	2 days
(anthracene-9-carboxylate)$_4$Mo$_2$	1 year
(benzoate)$_4$Mo$_2$	2 months
(thiophene-2-carboxylate)$_4$Mo$_2$	1 year
(furan-2-carboxylate)$_4$Mo$_2$	2 months

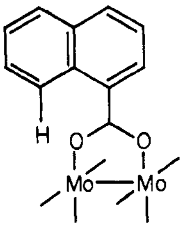
Compounds where steric factors hinder bonding coaxial to the metal-metal bond are generally far more air stable than those without such factors. This is well illustrated by comparison of the complexes derived from o- and p-toluenecarboxylic acid represented as II and III. It has been shown that electron pair donors such as pyridine can bind the molybdenum ions at sites coaxial to the metal-metal bond.[14] Models indicate that steric interaction of ortho CH_3 groups of II ensures that they will be on both sides of the dimolybdenum unit; therefore, it will be much more difficult to bring a donor within bonding distance of II than of III. Accordingly, III is oxidized within a few hours while II is unaffected over several months. A similar effect is noted with o- and p-chlorobenzoates. Likewise the 1-naphthylenecarboxylate derivative, IV, is indefinitely stable while the less hindered 2-naphthoate, V, is reactive. The anthracene-9-carboxylate, VI, was prepared because models show the dimolybdenum unit to be virtually encapsulated. It is unaffected by 1 year of exposure.



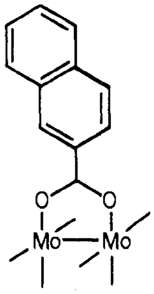
II



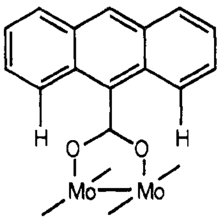
III



IV



V



VI

Many objections justly may be raised to conclusions drawn from this type of observation. For example it may be argued that differences in crystallization energy are responsible for these differences in reactivity. Two factors argue against this. First, the ortho compound would have to be stabilized over the para by its forming the stronger crystal. Such thermodynamic stabilization is improbable because in the cases of ortho *vs.* para CH_3 and Cl and in the cases of the 1- and 2-naphthoates the carboxylate which best hinders the axial site also forms the most soluble complex. This is an indication that these axially hindered complexes actually form weaker crystals. Second, from the kinetic point of view, a difference in crystal structure might be expected to result in a difference in the rate of the heterogeneous oxidation we are observing. In other words, the crystal packing of the axially hindered complexes would result in a much higher energy for the activated complex of oxidation. This possibility also appears unlikely because the solutions of the axially hindered complexes are all relatively air stable compared to other molybdenum(II) carboxylates. Once again, the problems of solubility mentioned above preclude a quantitative measurement of these effects; however, solutions of dimolybdenum(II) carboxylates such as the benzoate, acetate, and p-toluate are oxidized within seconds after exposure to

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(14) F. A. Cotton and J. G. Norman, *J. Amer. Chem. Soc.*, 94, 5697 (1972).

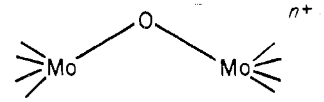
air while solutions of the axially hindered species such as the *o*-toluate or *o*-chlorobenzoate require several minutes to be oxidized.

Steric factors are not the only ones influencing the decomposition of dimolybdenum(II) carboxylates. There is also an important resonance factor. For example the benzoate is stable for weeks in air while the *p*-toluate decomposes in minutes and the *p*-methoxy compound is equally unstable. One might presume that this indicates the electron-donating groups destabilize and relatively electron-withdrawing groups will stabilize; however this is not the case because the *p*-chlorobenzoate is about as unstable as the *p*-toluate and the *p*-nitrobenzoate compound is too unstable to isolate.

It is tempting to speculate that axial site coordination is prerequisite to oxidation of dimolybdenum(II) complexes. Other studies have shown that such coordination lengthens and weakens the metal-metal bond;[14] however, kinetic studies will be required to determine this point.

Mass Spectral Studies. The dimolybdenum(II) carboxylates sublime congruently to give mass spectra with dominant molecular ion peaks. The large number of abundant isotopes for molybdenum and the presence of two molybdenum atoms in the molecule lead to a molecular ion which gives 15 different peaks with distinctive ratios one to another. This is illustrated in Figure 1. The pattern is a convenient "fingerprint" for any compound with the Mo_2^{4+} unit and no other atoms with two or more important isotopes. In the mass spectrum, overlap of these patterns occurs occasionally. In this instance the relative abundances of the two fragments may be arrived at by simultaneous equations for the intensity at several mass numbers using the expected relative intensities in Figure 1. The mass spectrum of tetra-μ-acetato-dimolybdenum(II) appears as Table III. Masses of ions refer to the ion in which the total molybdenum mass is 182 amu. In this case and in all the cases we have investigated, the molecular ion is the most abundant one. Also, no fragments are observed corresponding to ions containing a single molybdenum ion, consistent with but not proof for the great strength of the multiple bond.

For coordination compounds it has been demonstrated that prominent ions in the mass spectrum frequently are associated with species having the metal ion in its most common oxidation states.[6-12] The data in Table III show that oxidation states for the molybdenum ions of 2+, 2.5+, and 3+ are readily encountered. This is in keeping with the known chemistry of the binuclear molybdenum unit. The 2+ state is, of course, well known. Recently the compound $K_3Mo_2(SO_4)_4$ has been prepared and the net 2.5+ per molybdenum has been demonstrated.[15] Binuclear Mo(III) has also been shown to exist in solid halides such as $Mo_2Cl_9^{3-}$.[16] The higher oxidation states observed in fragments without any acetate ligands may in fact contain oxo-bridged molybdenum atoms as in VII. Many higher valent oxo-bridged molybdenum compounds are known.



VII

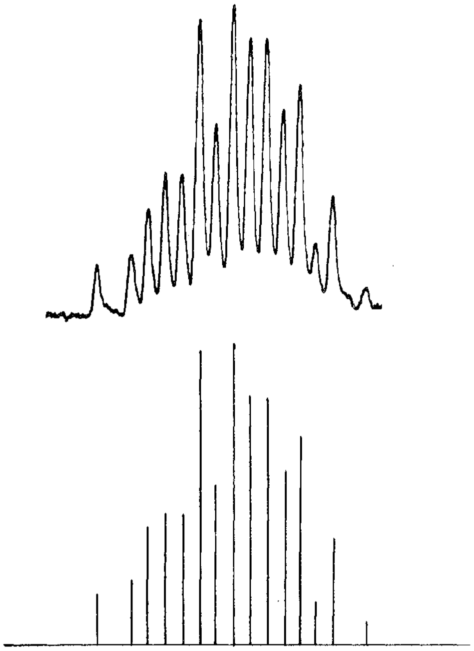


Figure 1. Observed (top) and calculated (bottom) isotope ratios for the mass spectrum of the molecular ion of tetra-μ-acetato-dimolybdenum(II).

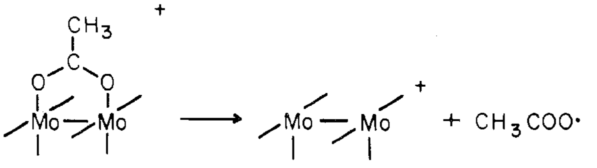
Table III. Mass Spectrum of Tetra-μ-acetato-dimolybdenum(II)[a]

m/e	Species	Oxidn state per Mo	Rel abund
428	$Mo_2Ac_4^+$	2.5	100
386	$Mo_2Ac_3OH^+$	2.5	3
385	$Mo_2Ac_3O^+$	3	4
369	$Mo_2Ac_3^+$	2	22
343	$Mo_2Ac_2OOH^+$	3	15
326	$Mo_2Ac_2O^+$	2.5	30
301	$Mo_2AcO(OH)_2^+$	3	16
284	$Mo_2AcO(OH)^+$	2.5	15
283	$Mo_2AcO_2^+$	3	12
268	Mo_2AcOH^+	1.5	28
267	Mo_2AcO^+	2	
257	$Mo_2AcO_3OH^+$	4	16
256	$Mo_2O_4^+$	4.5	15
240	$Mo_2O_3^+$	3.5	10
224	$Mo_2O_2^+$	2.5	3

[a] Ions listed are those with molybdenum atom weights totaling 192 amu. Ac = Acetate.

The molecular orbital theory of the quadruple bond has as its weakest component δ-orbital formation from d_{xy} orbitals on each of the molybdenum atoms.[17,18] The prevalence of molybdenum oxidation states of 2.5 and 3 in these fragmentation patterns may support the concept of the weakness of this component of the bond. The near absence of oxidation states less than 2 indicates that although stable binuclear compounds may be formed by oxidation of dimolybdenum(II) carboxylate complexes, they may not be formed by reduction.

The fragmentation patterns for the alkylcarboxylates are quite interesting. They provide evidence that molybdenum ion oxidation states are confined to the range of 2-3. Three major pathways (eq 1-3) for fragmentation are evident.



(1)

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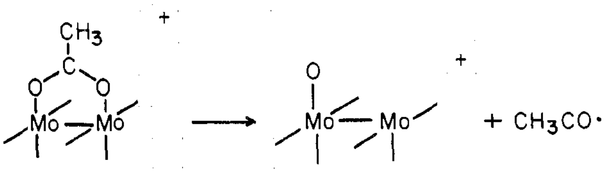
(15) F. A. Cotton, B. A. Frenz, and T. R. Webb, *J. Amer. Chem. Soc.*, 95, 4431 (1973).

(16) M. J. Bennett, J. V. Brencic, and F. A. Cotton, *Inorg. Chem.*, 8, 1060 (1969).

(17) F. A. Cotton, *Inorg. Chem.*, 4, 334 (1965).

(18) L. Dubicki and R. L. Martin, *Aust. J. Chem.*, 22, 1571 (1969).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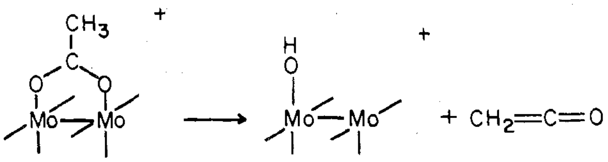
(3)

These are not independent of one another and the data indicate that none may succeed itself. For example, two successive or simultaneous losses of $CH_3COO\cdot$, $CH_3CO\cdot$, or $CH_2{=}C{=}O$ are not observed. A particularly striking case in point is the fragmentation which may be represented as (4).

$$\begin{tikzcd}
 & \underset{(385)}{Mo_2Ac_3O^+} \arrow[dr] & \\
\underset{(428)}{Mo_2Ac_4^+} \arrow[ur] \arrow[dr] & & \underset{(343)}{Mo_2Ac_2OOH^+} \\
 & \underset{(386)}{Mo_2Ac_3OH^+} \arrow[ur] &
\end{tikzcd} \qquad (4)$$

Even though the 385 and 386 species are observed with nearly equal intensity, only species 343, the mixed OH, O ion, is detected and nothing is observed corresponding to O_2 or $(OH)_2$ type fragments.

To an extent, the failure of any one fragmentation to succeed itself may be viewed as a reflection of the narrow range of oxidation states open to the binuclear unit. Reactions 1 and 2 result, respectively, in a reduction and an oxidation of the binuclear unit. These may not succeed themselves because that would lead to an unfavorable oxidation state, one which is outside the range of 2+ to 3+. Reaction 3 leaves the binuclear unit in the same oxidation state. It is, however, not a highly favored path of decomposition as the low abundance of *m/e* 386 shows. Thus, cases where it succeeds itself will have very low relative abundance and be swamped by other fragments. Tables IV and V contain the mass spectra of the propionate and the formate. The propionate is quite analogous to the acetate both in the type of fragments and in their relative abundance. The formate, however, is remarkably different. Most striking is the major fragment due to loss of CO_2. This must be arrived at by a migration of a formate hydrogen to one of the molybdenum atoms. This is remarkable for the distance the hydrogen must travel. No loss of $CHCOO\cdot$ is observed and so the hydrogen transfer must be very efficient. The mechanism in reaction 5 presents a scheme to rationalize this mode of fragmentation.

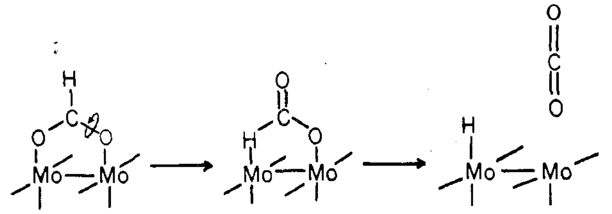
(5)

Table IV. Mass Spectrum of Tetra-μ-propionato-dimolybdenum(II)[a]

m/e	Species	Rel abund	*m/e*	Species	Rel abund
484	Molecular ion	100	315	$MoPrO(OH)_2^+$	10
470	CH_2 loss	1	298	Mo_2PrOOH	10
428	$Mo_2Pr_3OH^+$	1	297	Mo_2PrO_2	15
427	$Mo_2Pr_3O^+$	1	256	Mo_2O_4	20
411	$Mo_2Pr_3^+$	5	240	Mo_2O_3	5
371	$Mo_2Pr_2OOH^+$	2	224	Mo_2O_2	1
354	$Mo_2Pr_2O^+$	15			

[a] Ions listed are those with molybdenum atom weights totaling 192 amu. Pr = Propionate.

Table V. Mass Spectrum of Tetra-μ-formato-dimolybdenum(II)[a]

m/e	Assignment	Rel abund	*m/e*	Assignment	Rel abund
372	Molecular ion	100	269	$Mo_2FormO_2^+$	8
328	$Mo_2Form_3H^+$	90	256, 257	$Mo_2O_4^+$, $Mo_2O_3OH^+$	25
298	$Mo_2Form_2O^+$	75	240,241	$Mo_2O_3^+$, $Mo_2O_2OH^+$	12
277	$Mo_2FormOOH^+$	10			

[a] Ions listed are those with molybdenum atom weights totaling 192 amu. Form = Formate.

Some of the arylcarboxylates were also examined. These were disappointing. Little information on the Mo_2^{4+} unit was obtained from these complexes because the fragmentation patterns consist almost entirely of the molecular ion and but a few conventional fragmentations of one of the aromatic rings.

Conclusions

1. Dimolybdenum(II) aryltetracarboxylates display a wide variation in air stability depending on the nature and position of ring substituents.
2. Steric factors inhibiting coordination at the axial sites of the Mo_2^{4+} units stabilize these compounds against oxidation.
3. Possible valence states for the molybdenum ions of molybdenum carboxylates are 2+ and 3+, with lower valences improbable with carboxylate-type ligands.
4. Mass spectra of these compounds are consistent with their formulation as strong multiple bonds with one weak component.

Acknowledgments. The authors are pleased to acknowledge support of this research by the Research Corp. and the CUNY Faculty Research Awards Program. We also wish to express our gratitude to Professor R. H. Wiley for his assistance and patience in obtaining the mass spectra.

Registry No. (*o*-Methylbenzoate)$_4$Mo$_2$, 51329-42-1; (1-naphthoate)$_4$Mo$_2$, 51329-44-3; (2-naphthoate)$_4$Mo$_2$, 51329-45-4; (*p*-chlorobenzoate)$_4$Mo$_2$, 33637-85-3; (*o*-chlorobenzoate)$_4$Mo$_2$, 51329-43-2; (anthracene-9-carboxylate)$_4$Mo$_2$, 51329-46-5; (thiophene-2-carboxylate)$_4$Mo$_2$, 51329-47-6; (furan-2-carboxylate)$_4$Mo$_2$, 51329-48-7; (*p*-fluorobenzoate)$_4$Mo$_2$, 24329-23-5; (*p*-methylbenzoate)$_4$Mo$_2$, 33637-86-4; (benzoate)$_4$Mo$_2$, 24378-22-1; (acetate)$_4$Mo$_2$, 14221-06-8; (propionate)$_4$Mo$_2$, 41880-55-1; (formate)$_4$Mo$_2$, 51329-49-8.