SOME OXIDATION REACTIONS OF MOLYBDENUM(II) CARBOXYLATE DIMERS

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Some oxidation reactions of molybdenum(II) carboxylate dimers

by

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ABSTRACT*

Reactions of molybdenum(II) carboxylate dimers, $\text{Mo}_2(\text{O}_2\text{CR})_4$, with a variety of oxidizing agents were carried out. Crystalline products could be isolated upon reacting the carboxylates with iodine at room temperature. These new compounds were analyzed and were studied by a variety of physical methods, and it was discovered that single-electron oxidations had been carried out upon the carboxylate dimers. Results of the physical investigations are reported and are discussed with respect to the structures and compositions of the iodide derivatives.

Reactions of the carboxylate dimers with oxidizing agents other than iodine apparently failed to give oxidized dimeric products. Results of the reactions are presented, and conditions apparently necessary to allow isolation of oxidized species are considered.

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INTRODUCTION

The existence of compounds containing quadruple metal-to-metal bonds has been known for several years. One might attempt to predict certain aspects of the chemistry of such compounds by considering the metal-to-metal bond as analogous to the carbon-to-carbon multiple bonds found in organic chemistry. Such an interpretation would suggest that reactions of quadruply-bonded species with halogens would result in addition of halogen across the metal-to-metal bond, and lowering of the formal bond order from four to three. However, preliminary studies carried out¹ on molybdenum(II) carboxylate dimers suggested that reactions with iodine led instead to triiodide derivatives, $\text{Mo}_2(\text{O}_2\text{CR})_4\text{I}_3$.

The purpose of the work reported herein was to prepare and characterize a number of these iodide derivatives with a view towards obtaining as much information as possible about their structures and bonding. The reactivities of molybdenum(II) carboxylate dimers toward other oxidizing agents was also studied in the hope that such experimentation would yield fruitful information about the chemistry of quadruple metal-to-metal bonds.

Review of Previous Work

The following review of literature will be divided into three sections: (1) Syntheses and structures of quadruply-bonded metal species; (2) Theories regarding the nature of

the metal-metal quadruple bond; and (3) The oxidation chemistry of quadruply-bonded species.

Syntheses and Structures of Quadruply-Bonded Metal Dimers.-

The existence of metal-metal quadruple bonds was first postulated^{2,3} by Cotton and his co-workers in 1964, as an interpretation of the newly-elucidated structure⁴ of $\text{K}_2\text{Re}_2\text{Cl}_8$. This compound had been prepared⁵ by the reaction of potassium perrhenate with hydrogen and concentrated hydrochloric acid in a glass-lined steel bomb. The crystal structure of the product revealed a number of unexpected properties. The $[\text{Re}_2\text{Cl}_8]^{2-}$ anion could be regarded as two parallel, square-planar " ReCl_4^- " units, with the Re-Re distance a surprisingly short 2.24 Å. The eight chlorine atoms were arranged in an eclipsed fashion about the rhenium atoms. Based upon this structure, Cotton proposed the existence of a quadruple bond, having σ , π and δ components, between the two Re atoms. A more detailed description of his proposed bonding scheme will be found later in this review; however, it should be noted here that the existence of a bond of order four would predict an extremely short metal-metal distance, while the angular dependence of the δ component of such a bond would dictate the eclipsed configuration observed for the eight halogen atoms.

In addition to $\text{K}_2\text{Re}_2\text{Cl}_8$, Cotton and his co-workers were able to prepare a number of other salts of $[\text{Re}_2\text{Cl}_8]^{2-}$ and of its bromo analog.⁵ The similarity of the physical properties

of $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{Re}_2\text{Br}_8]^{2-}$, together with the fact that the bromo anion was readily formed from the chloro anion by halogen exchange,⁶ provided evidence that the quadruply bonded dimeric structure was preserved for this species as well.

It was also discovered that carboxylate derivatives of the general formula $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$, previously reported by Taha and Wilkinson,⁷ could be prepared more easily and in virtually quantitative yield by reacting the $[\text{Re}_2\text{X}_8]^{2-}$ ions with the appropriate carboxylic acids.⁵ A structural investigation led to the publication, in 1968, of the structure of dichlorotetrabenzoatodirhenium(III).⁸ In this structure, pairs of Re atoms were held together by four bridging carboxylate groups, with a chlorine atom terminally bonded to each metal atom. With the exception of the terminal chlorine atoms, the structure was similar to the $[\text{Re}_2\text{X}_8]^{2-}$ structure; the carboxylate oxygens occupied positions analogous to those of the 8 halogens in the $[\text{Re}_2\text{X}_8]^{2-}$ structure. The metal-metal distance was 2.235 Å, in excellent agreement with the distance of 2.24 Å found for $[\text{Re}_2\text{Cl}_8]^{2-}$.

Cotton and his co-workers felt that a quadruple bond existed between the two Re atoms in the benzoate derivative. Supporting evidence was provided by the similarity of its structure to that of $[\text{Re}_2\text{Cl}_8]^{2-}$, including the extremely short metal-metal bond. The distances between the rhenium atoms and the terminal chlorines was unexpectedly long; this was taken as evidence for weakening of the metal-chlorine bonds due to

a strong metal-metal interaction. The facility of interconversion between the $[\text{Re}_2\text{X}_8]^{2-}$ species and the carboxylate derivatives was regarded as the best evidence for retention of the metal-metal quadruple bond.

The existence of quadruple metal-to-metal bonding is by no means restricted to compounds of rhenium. Compounds involving quadruple molybdenum-to-molybdenum bonds are of the greatest importance to the work described in this thesis and the great preponderance of the discussion will be limited to these; however, representative compounds of a number of other metals will be mentioned briefly here.

In 1963, Eakins, Humphreys and Mellish⁹ reported the preparation of a compound of the formulation $(\text{NH}_4)_3\text{Tc}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$, by the zinc reduction of $(\text{NH}_4)_2\text{TcCl}_6$ in hydrochloric acid. The characterization of this product was undertaken by Bratton and Cotton,^{10,11} who found that the compound possessed $[\text{Tc}_2\text{Cl}_8]^{3-}$ groups essentially isostructural with $[\text{Re}_2\text{Cl}_8]^{2-}$. The metal-metal distance was 2.13 Å. The new species $[\text{Tc}_2\text{Cl}_8]^{3-}$, was not isoelectronic with $[\text{Re}_2\text{Cl}_8]^{2-}$, but since the two species were isostructural and since the Tc-Tc distance was short enough to suggest a very strong metal-metal bond, it was felt that the extra electron must reside in a non-bonding orbital rather than in a metal-metal antibonding orbital. Magnetic measurements were consistent with the presence of one unpaired electron per $[\text{Tc}_2\text{Cl}_8]^{3-}$ ion.

A fair number of compounds of chromium have been found to display the dimeric, quadruply bonded structure. The existence of hydrated chromium(II) acetate, $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$, has been known since 1844¹² and compounds of the same stoichiometry have been prepared using a number of other carboxylic acids.¹³ A structural examination of the acetate was performed by Cotton and his co-workers in 1970.^{14,15} The compound was found to be isostructural with copper(II) acetate dihydrate, and also with the $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$ species, in which pairs of metal atoms are bridged by the four carboxylate groups, with a terminal water molecule bound to either end along the metal-metal axis. The chromium-chromium distance was found to be 2.36 Å, and the compound was essentially diamagnetic. Since Cr(II) is isoelectronic with Re(III), this structural and magnetic information could be taken as evidence for the existence of a quadruple chromium-to-chromium bond.

Kurras and Otto¹⁶ prepared a compound formulated $\text{Li}_2\text{Cr}(\text{CH}_3)_4 \cdot 2\text{THF}$ by the direct reaction of CrCl_2 with LiCH_3 in tetrahydrofuran at -18°C . The structure was investigated by Krausse, Marx and Schödl,¹⁷ who found $\text{Cr}_2(\text{CH}_3)_8^{4-}$ groups isostructural with the previously known $[\text{Re}_2\text{X}_8]^{2-}$ and $[\text{Tc}_2\text{X}_8]^{3-}$ ions. The chromium-to-chromium distance was found to be 1.98 Å, and a quadruple metal-metal bond was again postulated. Krausse and Schödl¹⁸ also investigated the structure of $\text{Li}_4\text{Cr}_2(\text{C}_4\text{H}_8)_4 \cdot 4\text{C}_4\text{H}_{10}\text{O}$. This structure was very similar to

that of the methyl compound; two bidentate butyl groups were coordinated to each chromium atom and the metal-metal distance was $1.975 \text{ \AA}$. This compound also was postulated to contain a quadruple metal-metal bond.

Quadruply-bonded molybdenum dimer units are rather commonly found in the literature. Stephenson, Bannister and Wilkinson¹⁹ prepared a large number of compounds of stoichiometry $\text{Mo}_2(\text{O}_2\text{CR})_4$ by the reaction of molybdenum carbonyl with the appropriate carboxylic acids, and their anhydrides, if available. The reactions were carried out, either in the neat acid or in refluxing diglyme. Similarities in the infrared spectra of these compounds suggested that they possessed similar molecular structures. The structure of the acetate, $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, was investigated by Lawton and Mason²⁰ and was found to involve dimeric molybdenum units with the four carboxylate groups bridging the two metal atoms. The structure was very similar to those found for $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$ and the $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$ compounds, except for the absence of terminal ligands. The molybdenum-molybdenum distance was a surprisingly short $2.11 \text{ \AA}$, and, since Mo(II) also is isoelectronic with Re(III), a quadruple metal-to-metal bond was postulated for the molybdenum carboxylates. Cotton and Norman determined the structures of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ ²¹ and its bipyridine adduct, $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{C}_5\text{H}_5\text{N})_2$.²² Both compounds displayed the dinuclear, carboxylate bridged structure previously found for

$\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$; the pyridine molecules in the adduct were bonded through nitrogen atoms to either end of the molybdenum-molybdenum bond. The molybdenum-molybdenum distance in the parent compound was $2.09 \text{ \AA}$, while that in the pyridine adduct was $2.129 \text{ \AA}$. The molybdenum-nitrogen distance in the pyridine adduct was found to be a surprisingly long $2.548 \text{ \AA}$. The longer metal-metal bond distance in the adduct was taken as evidence that the metal-metal bond is somewhat weakened by axial co-ordination, while the unexpectedly long molybdenum-nitrogen distance was regarded as a measure of the extreme strength of the quadruple metal-metal bond.

In 1969, Brencic and Cotton reported the preparations of $\text{K}_4\text{Mo}_2\text{Cl}_8$ ^{23,24} and $[\text{enH}_2]_2[\text{Mo}_2\text{Cl}_8] \cdot 2\text{H}_2\text{O}$.²⁵ Both compounds were prepared by the reaction of hydrochloric acid and the appropriate salt with $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, in analogy with the preparations of $[\text{Re}_2\text{X}_8]^{2-}$ from $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$. Structural investigations of both compounds were carried out, revealing that both contained $[\text{Mo}_2\text{Cl}_8]^{4-}$ ions, isostructural with $[\text{Re}_2\text{X}_8]^{2-}$. Molybdenum-molybdenum distances were $2.139 \text{ \AA}$ for the potassium salt and $2.134 \text{ \AA}$ for the amine salt, both distances being close to the distance of $2.11 \text{ \AA}$ found for the parent $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. It was felt that steric requirements, in particular the necessity for minimizing chlorine-chlorine repulsions and for maintaining Cl-Mo-Cl angles near 90 degrees, provided sufficient explanation for the difference in molybdenum-molybdenum dis-

tance, and that no difference in bonding was implied. Brencic and Cotton also prepared and investigated $(\text{NH}_4)_5\text{Mo}_2\text{Cl}_9 \cdot \text{H}_2\text{O}$,²⁶ which consisted of $[\text{NH}_4]^+$, $[\text{Cl}]^-$, and $(\text{Mo}_2\text{Cl}_8)^{4-}$ ions rather than containing $[\text{Mo}_2\text{Cl}_9]^{5-}$ species. In this compound, the molybdenum-molybdenum distance was 2.15 Å.

San Filippo and co-workers have reacted $[\text{Mo}_2\text{X}_8]^{4-}$ and $[\text{Re}_2\text{Cl}_8]^{2-}$ with several phosphorus,²⁷ nitrogen, oxygen and sulfur²⁸ donor ligands to obtain complexes formulated $\text{Mo}_2\text{X}_4\text{L}_4$ and $\text{Re}_2\text{Cl}_6\text{X}_2$ (monodentate ligands) or $\text{Mo}_2\text{X}_4\text{L}_2$ (bidentate ligands). Nuclear magnetic resonance studies²⁷ carried out on a series of phosphine and phosphite complexes of rhenium and molybdenum were consistent with the familiar dinuclear structure in which each metal atom is surrounded by four coordinated groups and in which the ligands on the two metal centers are eclipsed. No X-ray structures were carried out, but spectral data suggested structures in which each metal is co-ordinated to two chlorine atoms and two phosphorus ligands, with phosphorus atoms trans to one another. Infrared and visible spectra of complexes of nitrogen, sulfur and oxygen donor ligands also suggested retention of the dinuclear Mo_2 unit. Some further structural conclusions could be drawn from the spectra, but no detailed structural information was available for any of the complexes.

Cotton and co-workers were able to prepare $\text{Li}_4[\text{Mo}_2(\text{CH}_3)_8] \cdot 4\text{THF}$ ²⁹ by the reaction of either $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ or

$\text{MoCl}_3(\text{THF})_3$ with LiCH_3 in diethyl ether-THF mixtures. Chemical evidence for the retention of a dinuclear structure was provided by the regeneration of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ upon reaction of $\text{Li}_4[\text{Mo}_2(\text{CH}_3)_8] \cdot 4\text{THF}$ with acetic acid at -78°C . The compound was examined crystallographically and found to contain $[\text{Mo}_2(\text{CH}_3)_8]^{4-}$ ions, isostructural with the previously known $[\text{Cr}_2(\text{CH}_3)_8]^{4-}$.¹⁷ The molybdenum-molybdenum distance was $2.148 \text{ \AA}$.

Previous work by Cotton and co-workers had involved the preparation and study of tetraallyldimolybdenum, $\text{Mo}_2(\text{C}_3\text{H}_5)_4$.³⁰ The compound could be prepared either by the reaction of molybdenum pentachloride with allylmagnesium chloride in ether³⁰ or by the reaction of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ with allyllithium, also in ether.²⁹ The structure was quite striking, involving pairs of molybdenum atoms co-ordinated to both terminal and bridging allyl groups. The two bridging allyl groups in the structure were exactly symmetrical; the carbon-carbon distances in these were all nearly identical. The terminal allyl group on each metal atom was also bonded in a symmetrical fashion; the carbon-carbon bonds in these groups were of nearly equal length, and the six molybdenum-to-carbon distances were also nearly identical. The molybdenum-molybdenum distance was $2.18 \text{ \AA}$. The structure was identical to that previously found for $\text{Cr}_2(\text{C}_3\text{H}_5)_4$.^{31,32} Although the molybdenum-molybdenum distance found for $\text{Mo}_2(\text{C}_3\text{H}_5)_4$ was longer than for

any of the compounds mentioned earlier, and although the allyl compound was of lower symmetry, a quadruple molybdenum-to-molybdenum bond was postulated for this species. It was felt²⁹ that steric requirements imposed by the presence of bridging allyl groups perhaps dictated the longer metal-metal bond.

In 1973, Ricard, Karagiannidis and Weiss³³ reported the synthesis and structure of the xanthate compound, $\text{Mo}_2(\text{S}_2\text{COC}_2\text{H}_5)_4 \cdot 2\text{THF}$. This compound was prepared by the reaction, at room temperature, of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ with potassium xanthate, in ethanol solution. The structure was very similar to that of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, involving pairs of molybdenum atoms bridged by four xanthate groups. The two solvent molecules were terminally co-ordinated to the dimeric unit and the molybdenum-to-molybdenum distance was $2.125 \text{ \AA}$, quite comparable to those found for the carboxylates.

The preparation of $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$, by the reaction of K_2SO_4 with $\text{K}_4\text{Mo}_2\text{Cl}_8$ in HSO_3CF_3 , was reported by Bowen and Taube in 1974.³⁴ The structures of this compound³⁵ and of the related $\text{K}_3\text{Mo}_2(\text{SO}_4)_4$ ³⁶ were examined by Cotton and his co-workers. The latter compound was prepared by allowing solutions of K_2SO_4 and $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$ to mix by diffusion. Both compounds displayed $\text{Mo}_2(\text{SO}_4)_4$ units, the pairs of molybdenum atoms being bound together by four bridging sulfates. The molybdenum-molybdenum distance in $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$ was $2.11 \text{ \AA}$ while that in $\text{K}_3\text{Mo}_2(\text{SO}_4)_4$ was $2.164 \text{ \AA}$. $\text{K}_3\text{Mo}_2(\text{SO}_4)_4$ was observed to be paramagnetic.

This was, therefore, a compound of great interest, being the first isolated example of a dimer in which a quadruple bond had been oxidized by one electron, with retention of the dimeric structure. The increase in metal-metal bond length was compatible with the decrease in bond order from 4 to 3.5, and the observed paramagnetism was consistent with the presence of an unpaired electron in the δ -bonding orbital.

While the chemistry of chromium and molybdenum shows many examples of quadruple metal-to-metal bonding, a similar tendency is lacking in the chemistry of tungsten. Although compounds of stoichiometry $W(O_2CR)_2$ have been reported,³⁷ no crystalline materials could be isolated for structural study. The only successful attempts to isolate a compound in which tungsten is involved in a quadruple bond have been those of Hoxmeier, Katovic and McCarley,³⁸ in which a mixed-metal dimer of the formulation $MoW(O_2CC(CH_3)_3)_4$ has been prepared. Further studies are in progress.

The preparation of one other mixed-metal dimer, $CrMo(O_2CCH_3)_4$ has also been reported,³⁹ although no detailed structural information was available.

Theories Regarding the Nature of Quadruple Metal-Metal Bonds.-

The first theoretical treatment of the quadruple metal-to-metal bond was published by Cotton and Harris,⁴⁰ concurrent with the publication of the $[Re_2Cl_8]^{2-}$ structure. The anion was regarded as two parallel ReX_4 groups connected only by

a rhenium-rhenium bond. The metal-metal axis was defined as the z axis. Metal orbitals s, p_x , p_y and $d_{x^2-y^2}$ were believed to participate in σ bonding to ligands, leaving the p_z , d_{z^2} , d_{xz} , d_{xy} , and d_{yz} orbitals for metal-metal bonding. A σ -bond was formed by overlap of the metal orbitals possessing σ symmetry (p_z and d_{z^2}). Orbitals possessing π symmetry with respect to the metal-metal axis were the d_{xz} and d_{yz} , and these gave rise to two π bonds. The d_{xy} orbitals, which possess δ symmetry with respect to the metal-metal axis, gave rise to the fourth component of the quadruple bond. It was postulated that the presence of this δ -bond constrained the quadruply-bonded system to an eclipsed configuration, since deviation from that configuration would sharply decrease the overlap of δ orbitals. Based upon the visible spectrum of $[\text{Re}_2\text{Cl}_8]^{2-}$ Cotton also inferred the existence of a pair of low-lying non-bonding orbitals, arising from the metal p_z and d_{z^2} orbitals, which were believed to be intermediate in energy between the δ and δ^* orbitals. A later extended-Hückel treatment⁴⁰ of $[\text{Re}_2\text{Cl}_8]^{2-}$ was in substantial agreement with this qualitative treatment, although the resulting energy-level diagram indicated one non-bonding orbital above and one below the δ^* orbital. Dubicki and Martin⁴¹ reported the results of a molecular orbital calculation carried out on $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. This treatment again gave rise to an energy-level diagram similar to that of Cotton and Harris,⁴⁰ although the two

orbitals arising from p_z and d_{z^2} metal orbitals were regarded as antibonding with respect to terminal ligands and were reversed in energy, and another antibonding orbital, arising from $d_{x^2-y^2}$ orbitals was found between the δ and the δ^* .

The most recent treatment of metal-metal quadruple bonds is that of Norman and Kolari,^{42,43} who employed the SCF- $X\alpha$ -SW method to $[\text{Mo}_2\text{Cl}_8]^{4-}$. Their predicted energy-level diagram was substantially different from those of Cotton and Harris⁴⁰ and Dubicki and Martin⁴¹ in that no non-bonding orbitals were found between the δ and δ^* orbitals. An antibonding orbital arising from metal $d_{x^2-y^2}$ orbitals was found somewhat above the δ^* orbital in energy.

It is interesting to note that all of the molecular orbital treatments mentioned above could be considered equivalent in terms of oxidation of a quadruply-bonded species. Each would predict the loss of electrons first from the δ orbital with concomitant lowering of the bond order to 3.5 and, barring large structural changes, the probable lengthening of the metal-metal distance.

However, the various theoretical treatments differ widely in terms of the predicted effects of adding additional electrons to a quadruply-bonded system. In the treatment of Cotton and Harris,⁴⁰ the lowest-lying orbital above the metal-metal δ orbital is non-bonding, and therefore population of this orbital by a one- or two-electron reduction should cause no significant structural effects. Dubicki and Martin⁴¹

located two antibonding orbitals (with respect to metal-ligand bonds) above the δ bonding orbital. In theory therefore, population of these orbitals, while not affecting the metal-metal bond, should decrease the strength of metal-to-ligand bonding and might be expected to cause a lengthening of metal-to-ligand distances. However, this effect might be difficult to ascertain positively, since a decrease in formal metal oxidation state by reduction might be expected to produce a similar bond lengthening.

The treatment of Norman and Kolari,^{42,43} however, would predict a quite different result. Since the δ^* was the lowest unoccupied orbital in their energy level diagram, reduction of a quadruply-bonded system would be expected to have a drastic effect on the metal-metal bond. Based upon their energy-level diagram, two-electron reduction would be expected to negate the δ bond by filling the δ^* orbital and thus to lower the bond order to three.

In light of these predictions, it is interesting to examine the structures of two materials, $(\text{NH}_4)_3\text{Tc}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ ⁹⁻¹¹ and $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$.⁴⁴ The technetium compound, as previously discussed, contains $[\text{Tc}_2\text{Cl}_8]^{3-}$ anions, isostructural with $[\text{Re}_2\text{Cl}_8]^{2-}$ but with one additional electron. The rhenium compound contains pairs of $(\text{ReCl}_2(\text{PEt}_3)_2)$ units joined by a metal-metal bond. The ligands are eclipsed, with phosphorus atoms on each metal atom trans to one another, and the sym-

metry of each molecule is D_{2d} . The metal-metal bond distance is between 2.22 Å and 2.25 Å, although the compound contains two more electrons than $[Re_2Cl_8]^{2-}$. On the basis of their structures and metal-metal distances both compounds are believed to contain quadruple metal-to-metal bonds. At first glance therefore, these observations might be interpreted as supporting the theoretical treatments of Cotton and Harris⁴⁰ or Dubicki and Martin⁴¹ in preference to that of Norman and Kolari^{42,43} since they indicate that incorporation of additional electrons does not affect the metal-to-metal bond. However, such interpretation requires the not necessarily accurate assumption that the energy level ordering in the reduced species is the same as that in the oxidized species. In addition, it is not known how dependent the ordering of unoccupied levels might be on such variables as charge, nature of ligands or identity of metal atoms, which are not taken into account in the various calculations. Therefore it is probably premature to dismiss any of these treatments on the basis of the two structures cited, and considerable further work will probably be necessary before the ordering of energy levels in any of these systems can be stated with authority.

Oxidation Chemistry of Quadruply-Bonded Species.- Considerable work has been done in recent years to elucidate the nature and stability of oxidation products of quadruply-bonded metal dimers. Hochberg, Walks and Abbott⁴⁵ studied the mass spectra

of a number of alkyl and aryl carboxylates of molybdenum, $\text{Mo}_2(\text{O}_2\text{CR})_4$. In each case, the parent ion $[\text{Mo}_2(\text{O}_2\text{CR})_4]^+$ could be readily detected, giving hope that single electron oxidations could be performed on these species with retention of the dinuclear structure.

In their studies of the aqueous chemistry of Mo(II) and Mo(III), Bowen and Taube³⁴ succeeded in preparing $\text{Mo}_2(\text{en})_4\text{Cl}_4$, by the reaction of $\text{K}_4\text{Mo}_2\text{Cl}_8$ with ethylenediamine. When solutions of this compound were studied by cyclic sweep voltammetry, an oxidation wave was observed which proved to be irreversible, suggesting that oxidation of this species results in major structural changes. No oxidized species, therefore, was isolated.

Cotton and his co-workers⁴⁶⁻⁴⁸ have studied the redox chemistry of a number of quadruply-bonded species, both electrochemically and by electron spin resonance spectroscopy. In their examination of $[\text{Re}_2\text{X}_8]^{n-}$ and $[\text{Tc}_2\text{Cl}_8]^{n-}$,⁴⁶ they found that $[\text{Tc}_2\text{Cl}_8]^{2-}$ could be produced by the electrochemical oxidation of the previously-known $[\text{Tc}_2\text{Cl}_8]^{3-}$ in solution. Their results suggested that the new ion was diamagnetic, which is expected since it is now isoelectronic with $[\text{Re}_2\text{Cl}_8]^{2-}$, but no salts could be isolated since the species had a short lifetime in solution. Electrochemical reduction of $[\text{Re}_2\text{Cl}_8]^{2-}$ gave rise to a short-lived product, believed to be $[\text{Re}_2\text{Cl}_8]^{3-}$, of which, again, no salts could be isolated.

Further work in the same laboratory⁴⁷ concerned quadruply-bonded molybdenum dimers. Electrochemical oxidation of $\text{Mo}_2(\text{O}_2\text{CC}_3\text{H}_7)_4$ in acetonitrile, dichloromethane or ethanol gave rise to short-lived products believed to be $[\text{Mo}_2(\text{O}_2\text{CC}_3\text{H}_7)_4]^+$, which gave identical esr spectra. The esr spectra were indicative of a single unpaired electron, coupled to two equivalent molybdenum nuclei, with a g-value of 1.941. The irreversible nature of the oxidation waves suggested that the oxidized product was undergoing further reaction in solution. Electrochemical oxidation of $[\text{Mo}_2\text{Cl}_8]^{4-}$ gave rise to a very short-lived product, believed to be $[\text{Mo}_2\text{Cl}_8]^{3-}$, for which no esr spectra could be obtained. It is interesting to note that an ion of formulation $[\text{Mo}_2\text{Cl}_8]^{3-}$ is known and has been structurally characterized.⁴⁸ Its structure was found to differ from that of $[\text{Mo}_2\text{Cl}_8]^{4-}$; rather than the eclipsed configuration of eight chlorine atoms in the dimeric unit, the structure is that of a confacial bioctahedron, with one vacant site in the shared face. No speculation was made as to the configuration of the $[\text{Mo}_2\text{Cl}_8]^{3-}$ species thought to be electrochemically generated.

Cotton et al. also carried out further studies of $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$ and $\text{K}_3\text{Mo}_2(\text{SO}_4)_4$ including detailed structural characterization of both.⁴⁹ Examination of the anions $[\text{Mo}_2(\text{SO}_4)_4]^{4-}$ and $[\text{Mo}_2(\text{SO}_4)_4]^{3-}$ proved quite informative. The metal-metal distance in the oxidized species, as previously mentioned, was 0.05 Å longer than that in the reduced species, as would be

predicted by the removal of an electron from the metal-metal bond. In addition, the molybdenum-oxygen distances in $[\text{Mo}_2(\text{SO}_4)_4]^{3-}$ are distributed around an average value of 2.06 Å as compared to that of 2.26 Å in $[\text{Mo}_2(\text{SO}_4)_4]^{4-}$, an effect that would be predicted upon lowering of the formal oxidation state of the metal atoms. The solid-state epr spectrum of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4$ was measured and showed a signal at $g = 1.90$ which was interpreted as indicating the presence of a single unpaired electron. $[\text{Mo}_2(\text{SO}_4)_4]^{4-}$ and $[\text{Mo}_2(\text{SO}_4)_4]^{3-}$ were also shown to be related electrochemically; solutions of $[\text{Mo}_2(\text{SO}_4)_4]^{3-}$ could be generated, in fact, only by the electrochemical oxidation of solutions of $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$. It is interesting to note that, although $\text{K}_3\text{Mo}_2(\text{SO}_4)_4$ appeared to be air- and water-stable, stable solutions of the oxidized ion could be generated only under carefully controlled conditions, and its lifetime in solution was apparently quite short. This is quite a hopeful observation in terms of future isolation of oxidation and reduction products of known multiply-bonded species. Hopefully, many species which can be generated electrochemically might be isolated if conditions could be discovered in which they could be stabilized by precipitation from solution.

EXPERIMENTAL

Most of the compounds synthesized during the course of this work were sensitive in some degree to exposure to water and oxygen. To minimize decomposition, all materials were prepared either in vacuo, or under a nitrogen atmosphere, using standard Schlenk techniques. Unless otherwise noted, all products were stored in screw-capped vials, under nitrogen atmosphere, in a drybox equipped with a circulation system capable of excluding atmospheric moisture and oxygen.

Materials

Reagents.- Molybdenum hexacarbonyl, iodine, propionic acid, benzoic acid and pivalic acid were purchased from commercial sources and used without further purification.

Solvents.- Chlorobenzene, 1,2-dichloroethane, o-dichlorobenzene, toluene, decahydronaphthalene (decalin) and cyclohexane were purged with a stream of dry nitrogen for ten to thirty minutes immediately prior to use. Acetonitrile was dried over Molecular Sieves (Linde 4A) and purged with nitrogen prior to use. Benzene was refluxed over sodium, distilled into a fresh flask, and stored under argon or nitrogen prior to use.

Synthesis

Molybdenum(II) Carboxylates.- Molybdenum(II) carboxylates were prepared by the method of Stephenson, Bannister and Wilkinson,¹⁹ modified by Hoxmeier and McCarley.¹ Prepara-

tions of the benzoate and pivalate derivatives were very similar. In a typical preparation, 100 ml of either decalin or o-dichlorobenzene were brought to reflux in a Schlenk-type reaction vessel equipped with a reflux condenser. To the solvent was added 20 mmol of molybdenum carbonyl, together with a 10% excess of the appropriate carboxylic acid, and the mixture was allowed to reflux until gas evolution ceased. Bright orange crystals of the benzoate formed upon cooling the reaction mixture to room temperature; these were collected on a frit in air, washed with benzene and with cyclohexane and dried in vacuo. Slender yellow needles of the pivalate also were isolated at room temperature. They were collected on a frit under nitrogen, washed with cyclohexane and dried in vacuo. Tetrapropionatodimolybdenum(II) was most conveniently prepared by a two-step synthesis involving, as a first step, the isolation of $\text{Mo(CO)}_4(\text{tmen})$, where tmen is tetramethylethylenediamine. In a typical preparation, 13.2 g Mo(CO)_6 was placed in a reaction vessel along with 6.1 g tmen and 100 ml of toluene. The mixture was brought to reflux and allowed to reflux until gas evolution ceased. Large yellow crystals of $\text{Mo(CO)}_4(\text{tmen})$ formed upon cooling the mixture to room temperature; these were collected in air, washed with cyclohexane, and dried in vacuo. The propionate derivative, $\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4$, was prepared by the reaction of $\text{Mo(CO)}_4(\text{tmen})$ with neat propionic acid. Typically, 6.5 g $\text{Mo(CO)}_4(\text{tmen})$ was

placed in a reaction vessel along with 100 ml of neat propionic acid. The mixture was brought rapidly to reflux and allowed to reflux until gas evolution ceased. Yellow needles of $\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4$ were formed upon cooling the reaction mixture to 0°C ; they were collected on a frit under nitrogen and dried in vacuo.

Tetrapropionatodimolybdenum(2.5)Triiodide, $[\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4]^+\text{I}_3^-$.

In a typical preparation, 1.5 g (3.1 mmol) of $\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4$ and 1.3 g (5.2 mmol) of I_2 were placed in a Schlenk flask along with 50 ml of 1,2-dichloroethane. The mixture was stirred for one hour at room temperature. The brown microcrystalline product (85% yield) was collected on a frit in air, washed twice with 5 ml-portions of chlorobenzene and twice with 5-ml portions of cyclohexane, and dried in vacuo.

Anal. Calcd. for $\text{Mo}_2\text{C}_{12}\text{H}_{20}\text{O}_8\text{I}_3$: Mo, 22.19; I, 44.02, C, 16.66; H, 2.33. Found: Mo, 21.54; I, 43.83; C, 16.49; H, 2.49.

Tetrabenzoatodimolybdenum(2.5)Triiodide, $[\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4]^+\text{I}_3^-$.

Typically, 2.10 g (3.1 mmol) of $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ and 1.3 g (5.2 mmol) of I_2 were placed in a Schlenk flask along with 50 ml of 1,2-dichloroethane. The mixture was stirred at room temperature for one hour and then filtered in air, yielding the brown microcrystalline product in 96% yield. The product was washed with chlorobenzene and cyclohexane and dried in vacuo.

Anal. Calcd. for $\text{Mo}_2\text{C}_{28}\text{H}_{20}\text{O}_8\text{I}_3$: Mo, 18.15; I, 36.02; C,

49.72; H, 2.98. Found: Mo, 17.99, I, 36.36; C, 49.65; H, 3.05.

Tetrapivalatodimolybdenum(2.5)triiodide, $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+$

I_3^- .- In a typical reaction, 1.0 g (1.7 mmol) of $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$ was placed in a Schlenk flask along with 0.72 g (2.83 mmol) of iodine and 40 ml of either benzene or 1,2-dichloroethane. The mixture was stirred for 12 hours at room temperature and cooled for 2 hours at 0°C. The red-brown crystalline product was collected on a frit in air, washed with chlorobenzene and cyclohexane, and dried in vacuo. The yield of product was 80%. Anal. Calcd. for $\text{Mo}_2\text{C}_{20}\text{H}_{36}\text{O}_8\text{I}_3$: Mo, 19.64; I, 38.96; C, 24.58; H, 3.71. Found: Mo, 19.34; I, 38.85; C, 24.45; H, 3.89; I/Mo, 1.52.

Analytical Methods

Molybdenum.- Samples were decomposed with nitric acid and were ignited to molybdenum trioxide in tared porcelain crucibles.

Iodine.- Samples were dissolved in dilute $\text{KOH-H}_2\text{O}_2$ solution, boiled to decompose peroxides, acidified with acetic acid and titrated potentiometrically with standard silver nitrate solution. A Photovolt Digicord pH meter was used, equipped with a silver indicating electrode and a Beckman Model 90-02 Double-Junction Reference Electrode.

Carbon and Hydrogen.- Carbon and hydrogen analyses were per-

formed by Mr. J. J. Richard of Analytical Services Group I, Ames Laboratory, and by the Galbraith Microanalytical Laboratory, Knoxville, Tennessee.

Physical Measurements

Magnetic Susceptibility.- Magnetic measurements were made with a Faraday balance apparatus which has been described previously.⁵⁰ Measurements were made from 77°K to room temperature by the use of a cryostat equipped with a heater to warm the sample. Sample temperatures were determined by use of a copper-constantan thermocouple located near the sample. Samples were loaded in the drybox into a screw-topped Teflon bucket, which was then suspended between the pole faces from one arm of the electrobalance employed. Corrections for the diamagnetism of the sample bucket were made for each determination.

Vibrational Spectra.- Spectra of solid samples prepared as Nujol mulls were obtained using a Beckman Model 4250 spectrophotometer for the 1600-600 cm^{-1} range and a Beckman IR-11 spectrophotometer for the region below 600 cm^{-1} . In most cases, the samples were sufficiently stable to permit preparation of mulls outside the drybox. Spectra between 1600 and 600 cm^{-1} were obtained using cesium iodide windows, while polyethylene sheets were employed as windows for use below 600 cm^{-1} .

X-Ray Diffraction.- X-Ray powder diffraction patterns were recorded using a 114.59 mm Debye-Scherrer camera. Nickel-

filtered copper $K\alpha$ radiation was employed. Samples were finely ground, sealed into 0.2 mm Lindemann capillaries, and exposed to radiation for six to twelve hours.

Electron Spin Resonance Spectra.- Electron spin resonance spectra were obtained at room temperature on powdered samples in quartz ampoules. A Strand 601 spectrometer was used, with a Magnion magnet system and a locally constructed cavity. The spectra were calibrated with proton frequency marks at regular intervals during the linear field sweep.

RESULTS AND DISCUSSION

Synthesis

Preparation of the Molybdenum(II) Carboxylates.- A number of points appeared to be significant in the preparation of the molybdenum carboxylate starting materials. First, it proved necessary to bring the reactions to temperature very quickly. In particular for the high-temperature reactions using decalin or o-dichlorobenzene as solvent, it was essential that the mixtures reach reflux within two minutes after heating commenced. Failure to attain reflux temperatures rapidly resulted in drastically reduced yields and products heavily contaminated with a brown oxidation product which was not characterized.

Attempts to prepare $\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4$ by a one-step synthesis similar to that employed for $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ or $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$ yielded only a small amount of a very heavily contaminated product. This might be accounted for either by a decreased reactivity of propionic acid toward molybdenum carbonyl, or by an increased solubility of the propionate derivative, compared to the benzoate and pivalate, in o-dichlorobenzene.

It is interesting to note that reaction of pivalic acid with molybdenum carbonyl in o-dichlorobenzene appeared to give a different product from that of the analogous reaction carried out in decalin. Although the yellow crystals isolated from the two reactions seemed identical in appearance and reactivity, they gave dissimilar X-ray powder patterns. Lines were

observed at the following values of d ($\text{\AA}$) for the decalin product: 11.44s, 10.75s, 9.59s, 9.18w, 7.91w, 7.58w, 7.26w, 6.81s, 6.36m, 5.63w, 5.02s, 4.79w, 4.64s, 4.39s, 4.10w, 3.83w, 3.67w.

The following lines were observed for the o-dichlorobenzene product: 11.49w, 10.46s, 9.16s, 6.36s, 5.69m, 5.51m, 5.01s, 4.59s, 4.26w, 4.13m. The pivalate product prepared from o-dichlorobenzene appeared to be of somewhat higher purity than the decalin product and was therefore used in subsequent reactions. Debye-Scherrer patterns of $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ produced from o-dichlorobenzene and from decalin proved identical.

Preparation of the Iodide Derivatives.- Acetonitrile, 1,2-dichloroethane and benzene were employed as solvents for the preparation of iodide derivatives. For the pivalate system, reaction of the parent dimer with iodine in slight excess over an I/Mo ratio of 1.5 in either benzene or 1,2-dichloroethane produced the triiodide derivative, $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$, in reasonable yield. Reactions performed in acetonitrile, on the other hand, yielded no solid products.

For the propionate and benzoate systems, 1,2-dichloroethane appeared to be the best solvent for preparation of triiodide derivatives. Reactions in benzene appeared much slower and did not appear to proceed cleanly to the triiodide.

When $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ was reacted with large amounts of

iodine in acetonitrile, products with I/Mo ratios greater than 1.5 could be formed. Hoxmeier and McCarley¹ isolated a shiny black crystalline substance formulated $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{I}_5$ which appeared indefinitely stable when stored under vacuum. This preparation proved difficult to duplicate; however, attempts to prepare the product led to the isolation of a number of apparently homogeneous materials having I/Mo ratios ranging from 1.5 to 2.4. The materials with I/Mo ratios higher than 2.0 were invariably darker in color than those with ratios near 1.5, and appeared to be somewhat unstable with respect to loss of molecular iodine. Iodine loss could be seen upon washing these materials with common solvents, upon grinding them, or upon exposing them to heat or to prolonged evacuation. These observations were at first interpreted as indicating the existence of the compound $[\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4]^+\text{I}_5^-$, unstable with respect to decomposition into $[\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4]^+\text{I}_3^-$ and molecular iodine. However, in light of X-ray diffraction and magnetic data presented below, it became necessary to consider other possible formulations.

General Observations

Stabilities of the Iodide Derivatives.- The triiodide derivatives of $\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4$ and $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$ were fairly air-sensitive. Although they could be weighed quickly in air, loaded into capillaries, or ground into mulls, decomposition became noticeable if the compounds were allowed to stand in

air for over thirty minutes. In contrast, derivatives of $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ with iodine-to-molybdenum ratios near 1.5 appeared to be stable for months in air. These observed behaviors closely paralleled the stabilities of the parent dimers. Derivatives of $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ having iodine-to-molybdenum ratios near 2.5 were not especially stable, decomposing with evolution of molecular iodine within thirty minutes.

Solubilities of the Iodide Derivatives.- Triiodides of $\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4$ and $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$ were slightly soluble in benzene, chlorobenzene and 1,2-dichloroethane, but were insoluble in cyclohexane. Both compounds gave very dark brown solutions in acetonitrile, from which no solid could be recovered. Derivatives of $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ having iodine-to-molybdenum ratios near 1.5 had similar solubilities in benzene, chlorobenzene, 1,2-dichloroethane and cyclohexane, but their behavior in acetonitrile was strikingly different. When material of formulation $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{I}_3$ was stirred in acetonitrile at room temperature, a light-orange solid precipitated immediately. This solid was identified on the basis of elemental analysis and by its X-ray powder pattern as pure $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$. The yield of solid was found to be about 33%, independent of reaction time. No solid product could be isolated from the dark-brown mother liquor. Stirring the "triiodide" in absolute ethanol produced a similar result; an intense yellow solution formed again accompanied by the precipitation of

starting material. Derivatives having large ratios of iodine to molybdenum were not observed to decompose in this fashion in acetonitrile although they did so in absolute ethanol.

This anomalous behavior of the benzoate derivatives was at first thought to be an artifact of the comparative insolubility of the benzoate starting material in common solvents. It was felt that similar decomposition pathways might exist for all of the triiodides, but that only in the case of the benzoate was the starting material so insoluble as to precipitate from solution. Again, however, alternative explanations could be suggested on the basis of magnetic and esr data, as discussed below.

Characterization of the Iodide Derivatives

Infrared Spectra (1600cm^{-1} - 200cm^{-1}). - A comparison of the spectra of parent dimers and iodide derivatives over this region is of interest since the spectra may be used as a diagnostic tool in determining whether the dimeric structure is preserved upon oxidation with iodine. The region between 700cm^{-1} and 400cm^{-1} is of particular significance since vibrations consisting wholly or in part of molybdenum-oxygen stretching might be expected to lie in this region and these should be quite sensitive to changes in the molecular structure. Infrared data for the parent dimers and their iodide derivatives are compiled in Tables 1 through 3, and the spectra of $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$ and $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$ are

Table 1. Infrared frequencies (cm^{-1}) for $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$ and $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$ (200-1600 cm^{-1})^a

$\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$	$[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$
	230w
	290w
318w	--
340m	335m
420m	445sh
450s	465sh
615s	625s
775m	778m
795m	788m
895m	888m
935w	938w
975w	975w
1025w	1022w
1218s	1215s
1300w	1300sh
1362s	1365s
1420s	1420s
1485s	1485s
1550w	1570w

^aRelative intensities are indicated as s, strong; m, medium; w, weak; sh, shoulder.

Table 2. Infrared frequencies (cm^{-1}) for $\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4$ and $[\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4]^+\text{I}_3^-$ (200-1600 cm^{-1})^a

$\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4$	$[\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4]^+\text{I}_3^-$
250w	-
322m	325sh
340m	350s
420m	430sh
438m	445sh
590s	615s
604sh	-
675s	695s
808s	810s
888s	890m
1008m	1010m
1075m	1080m
1085m	1085w
1260w	1250w
1295s	1295s
1301s	-
1380m	1380m
1410sh	1400w
1435s	-
1450s	1440s
1512s	1520w

Table 3. Infrared frequencies (cm^{-1}) for $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ and $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{I}_3$ (200-1600 cm^{-1})

$\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$	$\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{I}_3$	$\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$	$\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{I}_3$
270m	260s	1030m	1025m
--	275w	1070m	1070m
315w	--	1100w	1095w
342w	350w	1140m	1140m
--	370w	1160w	1160w
360m	390sh	1290w	1290w
382m	400m	1310w	1310w
--	488sh	1320w	1320w
447m	495m	1405s	1405s
482s	512s	1440s	1440s
505sh	--	1450m	--
625w	--	1490s	1490s
665w	665w	1505sh	1505sh
680s	680s	1590m	1590sh
705s	710s	1600m	1600s
805w	805w		
840m	840m		
860w	845w		
930m	935w		
975w	975w		
1000w	1000w		

reproduced in Figures 1 and 2. It can be seen that the spectrum of each carboxylate dimer matches nearly perfectly, band for band, with that of its iodide derivative above 700 cm^{-1} . For the pivalate system, bands at 420, 450 and 615 cm^{-1} in the spectrum of the starting material correspond to bands located at 445, 465 and 625 cm^{-1} in the spectrum of the triiodide derivative. Shifts to higher frequencies would be predicted for molybdenum-oxygen bands upon oxidation of the dimeric unit, and therefore these bands were thought to contain significant contributions from molybdenum-oxygen stretching and to constitute evidence for oxidation, with retention of the dimeric structure. The band above 600 cm^{-1} was included because, even though it is probably too high in energy to be assigned as a pure molybdenum-oxygen stretching mode, its sensitivity toward oxidation suggests some contribution from such modes.

A similar pattern can be seen in the spectrum of the propionate compounds, where bands located at 590, 438 and 420 cm^{-1} in the spectrum of the starting material are replaced by bands at 615, 445 and 430 cm^{-1} in the spectrum of the triiodide. Similarly, the spectrum of $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ shows bands at 360, 382, 447 and 482 cm^{-1} , which correspond to bands at 390, 400, 495 and 512 cm^{-1} in the spectrum of a compound formulated $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)\text{I}_3$. Recording of infrared spectra of materials with I/Mo ratios greater than 2.0 proved impossible since

Figure 1. Infrared spectrum of $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$ from 1600-200 cm^{-1}

Figure 2. Infrared spectrum of $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$ from 1600-200cm⁻¹

rapid decomposition, accompanied by evolution of molecular iodine, was visible upon grinding the samples. A vibrational study of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ has been carried out,⁵¹ but it proved to be of somewhat limited value in assigning bands as it was restricted to the region below 400cm^{-1} . Bands at 338, 348 and 369cm^{-1} were assigned by the authors to Mo-O stretching. Although these frequencies are lower than those thought to contain contributions from Mo-O stretching in the propionate, pivalate and benzoate systems, the frequency shifts observed here upon oxidation constitute good evidence for the validity of the assignments made.

Electron Spin Resonance Spectra.- Spectra of crystalline powders were obtained for $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$, $[\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4]^+\text{I}_3^-$, for a material of composition $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{I}_3$, and for the compound formulated $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{I}_5$. The spectra of all of the samples were quite similar, each consisting of a single intense, narrow signal. Values of $\langle g \rangle$ calculated from the spectra for all of the samples were nearly identical; these are given in Table 4. The spectra bear a strong resemblance to the solid-state spectrum of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4$, reported by Cotton and co-workers,⁴⁹ which consisted of a single line with $\langle g \rangle = 1.91$. The spectrum of $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$ is reproduced in Figure 3.

From the value of g it is possible⁵² to calculate an estimated magnetic moment for each sample by use of the follow-

ing relationship:

$$\mu = g[S(S+1)]^{1/2}$$

For a system having a single electron, with $S = 1/2$, the relationship may be re-written:

$$\mu = g[0.75]^{1/2}$$

Values of μ were calculated and appear also in Table 4. The close similarity between values of $\langle g \rangle$ for all these samples is consistent with the assumption that the same species, the singly-oxidized dimer, is present in each.

Table 4. Electron spin resonance and magnetic data for the iodide derivatives

Sample	$\langle g \rangle$	μ_{calc}^a	μ_{obs}^b
$[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+ \text{I}_3^-$	1.935	1.676	1.67
$[\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4]^+ \text{I}_3^-$	1.935	1.676	1.60
$\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4 \text{I}_3$	1.936	1.677	1.34
$\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4 \text{I}_5$	1.938	1.678	--

^aCalculated from $\mu = g[S(S+1)]^{1/2}$.

^bFrom magnetic susceptibility measurements.

Figure 3. ESR spectrum of a solid sample of $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$

Magnetic Measurements.- In order to obtain further information concerning the electronic structures of the oxidized species, magnetic susceptibilities of the three triiodide compounds were measured over a wide temperature range. For each sample, adherence to the Curie law was inferred from the linearity of a plot of molar susceptibility versus reciprocal of temperature. For a system which obeys the Curie law, the magnetic moment may be calculated⁵³ from the slope of such a line by the Van Vleck equation:

$$\chi_M = \frac{N\beta^2\mu^2}{3kT} + \chi_D + \chi_{TIP}$$

The sum of the temperature independent paramagnetism and the diamagnetic correction is the intercept of such a plot. Slopes and intercepts used were those of lines generated by a least-squares fit of measured susceptibilities and temperatures to an equation of the form $Y = A + BX$. Magnetic data for the triiodides are summarized in Tables 5 through 7 and plots of χ_M versus $1/T$ are reproduced in Figures 4 through 6.

The magnetic moment of 1.67 observed for $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$ is in excellent agreement with the value estimated from its est spectrum. This provides strong supporting evidence for the formulation of this material as a single-electron oxidation product of $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$.

The benzoate system, however, was not so well-behaved. The value of 1.34 for its observed magnetic moment is sub-

Table 5. Magnetic susceptibility data for $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+ \text{I}_3^-$

T(°K)	$10^6 \chi_M$ (emu/mole)	T(°K)	$10^6 \chi_M$ (emu/mole)
125	2328	190	1421
131	2319	200	1333
140	2080	226	1137
151	1921	250	994
160	1788	273	895
170	1642	300	749
180	1530		
$10^6(\chi_D + \chi_{\text{TIP}}) = -394.36$			

Table 6. Magnetic susceptibility data for $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4 \text{I}_3$

T(°K)	$10^6 \chi_M$ (emu/mole)	T(°K)	$10^6 \chi_M$ (emu/mole)
129	1442	201	827.9
140	1307	225	699.7
160	1104	250	595.7
170	1026	275	513.7
180	950	300	443.6
190	885.4		
$10^6(\chi_D + \chi_{\text{TIP}}) = -305.8$			

Table 7. Magnetic susceptibility data for $[\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4]^+ \text{I}_3^-$

T(°K)	$10^6 \chi_M$ (emu/mole)	T(°K)	$10^6 \chi_M$ (emu/mole)
90	3342	150	1899
95	3164	160	1793
100	3010	180	1593
120	2464	200	1418
130	2221	225	1219
139	3090	302	839
$10^6(\chi_D + \chi_{\text{TIP}}) = -205.75$

Figure 4. Curie plot for $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$. Experimental points indicated by +. Solid line calculated by least squares fit

Figure 5. Curie plot for $[\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4]^+\text{I}_3^-$. Experimental points indicated by +. Solid line calculated by least-squares fit

Figure 6. Curie plot for $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{I}_3$. Experimental points indicated by +. Solid line calculated by least-squares fit

stantially lower than the calculated value of 1.677. Strict adherence of the sample to the Curie law over the temperature range studied tends to rule out the possibility that long-range magnetic coupling in the solid is responsible for the reduction in magnetic moment. One possible interpretation of the data would be the formulation of this material as a single phase containing a mixture of oxidized (paramagnetic) and unoxidized (diamagnetic) species. The phase could be formulated in general terms as:

where, in order to preserve the observed stoichiometry, the following relationship holds:

$$2c + b = 3(a+b)$$

It should be emphasized that this is merely a tentative formulation and that the actual composition of the species cannot at this point be stated with authority.

Assuming that the sample does consist of both oxidized and unoxidized dimers, it is possible to estimate their relative concentrations from magnetic and esr data. For a sample having m components, each with its own susceptibility, the measured bulk susceptibility χ_{meas} may be written:

$$\chi_{\text{meas}} = \sum_{a=1}^m \chi_a$$

In terms of molar susceptibilities χ_a^M of the components,

$$\chi_{\text{meas}} = \sum_{a=1}^m \chi_a^M n_a$$

where n_a is the number of moles of component a in the mixture.

An apparent molar susceptibility χ_{app}^M of the overall sample may be calculated by assuming a molecular weight MW_{app} . If the total weight of the sample is W_{tot} , then:

$$\chi_{\text{app}}^M = \chi_{\text{meas}} \left(\frac{MW_{\text{app}}}{W_{\text{tot}}} \right) = \left(\frac{MW_{\text{app}}}{W_{\text{tot}}} \right) \sum_{a=1}^m \chi_a^M n_a$$

If one writes

$$n_{\text{app}} = \frac{W_{\text{tot}}}{MW_{\text{app}}}$$

and converts to μ^2 on both sides of the equation, one may show:

$$\mu_{\text{app}}^2 = \frac{\sum_{a=1}^m \mu_a^2 n_a}{n_{\text{app}}}$$

For the benzoate system, one may consider only paramagnetic contributions and thus write:

$$\mu_{\text{app}}^2 = \frac{\mu_{\text{ox}}^2 n_{\text{ox}}}{n_{\text{total}}}$$

where $n_{\text{ox}}/n_{\text{total}}$ is the mole ratio of oxidized molybdenum dimers to total molybdenum dimers in the sample. Using the observed value of 1.34 as μ_{app} and 1.66 as μ_{ox} , it is possible to estimate a value of 0.65 for $n_{\text{ox}}/n_{\text{total}}$. It should be emphasized that this treatment is of general applicability since it assumes no particular composition for the oxidized species. In summary, then, one possible explanation for

the disparity between magnetic and esr measurements for $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{I}_3$ might be the formulation of the material as a mixture in which only 65% of the molybdenum dimers are oxidized.

For the propionate system, the measured magnetic moment of 1.60 is somewhat lower than the value of 1.68 calculated from the esr spectrum. While this deviation is not nearly so dramatic as that seen for the benzoate, it is interesting to apply a similar treatment to the propionate system. Treating the compound as was done for the benzoate would give a value of .93 for $n_{\text{ox}}/n_{\text{total}}$, or indicate that over 90% of the dimers present were oxidized.

Evidence which might tend to support the formulation of these two materials as mixed oxidation state phases is provided by the fact that, during the preparative stages of this work, apparently homogeneous iodide derivatives of $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ in particular could be isolated in which the iodine-to-molybdenum ratios deviated significantly from 1.5. This fact, plus the fact that derivatives of $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ having iodine-to-molybdenum ratios up to 2.5 exist, suggests the possibility that a whole range of mixtures of oxidized species, unoxidized species and molecular iodine may exist. Formulation of the benzoate derivatives as mixtures would also be in line with the anomalous precipitation of starting materials observed when the benzoate iodides are stirred in

various solvents. Further evidence in support of this suggestion is provided by X-ray data which are presented below.

The apparent differences in structure between iodide derivatives of the various carboxylates cannot be readily explained on the basis of currently available information. It is possible that, if detailed structural information might be obtained, accurate structures of the various derivatives might shed some further light on their behavior. However, in light of the microcrystalline nature of the compounds together with their anomalous behaviors in solution, such structural characterization may not be possible.

X-ray Diffraction Measurements.- Debye-Scherrer powder patterns were recorded for all of the starting materials and their iodide derivatives. No similarities could be detected between patterns of different carboxylates, indicating that they were not isomorphous. Not surprisingly, patterns arising from the iodide derivatives of the various carboxylates were also strikingly different. Values of d calculated from all of the patterns are given in Tables 8 through 10.

Strong similarities were noted between the powder patterns of $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{I}_3$ and of the compound earlier prepared,¹ formulated $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{I}_5$. In order to compare the powder patterns more accurately, samples of these two materials, together with a material of intermediate composition, having an I/Mo ratio of 2.4, were sealed into 0.3 mm Lindemann capillar-

Table 8. X-ray diffraction data for $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$ and $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$. Values of $d(\text{\AA})$

$\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4^a$	$\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4^b$	$[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$
11.44s	11.49w	8.33s
10.75s	10.46s	7.55s
9.59s	9.16s	6.64m
9.18w	6.36s	4.78m
7.92w	5.69m	4.55m
7.58w	5.51m	4.13m
7.26w	5.01s	2.89m
6.81s	4.59s	
6.36m	4.26w	
5.63w	4.13m	
5.02s		
4.79w		
4.64s		
4.39s		
4.10w		
3.83w		
3.67w		
2.77w		
2.71w		
2.32w		
s = strong, m = medium, w = weak.		

^aProduct prepared in decalin.

^bProduct prepared in o-dichlorobenzene.

Table 9. X-ray diffraction data for $\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4$,
 $\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4\text{I}_3$ and $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$. Values of $d(\text{\AA})$

$\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4$	$\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4\text{I}_3$	$\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$
9.80vw	10.21vw	11.14s
8.72s	7.18s	10.22s
6.21s	6.76m	7.53m
4.99s	4.62m	5.64m
4.42m	4.06w	5.09m
4.10s	3.90w	4.92m
3.64w	3.66m	4.63m
3.37w	3.59w	4.39w
2.93w		4.01w
2.87m		3.49s

Table 10. X-ray diffraction data for iodide derivatives of $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$. Values of $d(\text{\AA})$

I/Mo = 1.5	I/Mo = 2.4	I/Mo = 2.5
--	--	12.58vw
10.82s	10.70s	10.70s
--	--	9.82vw
7.23vs	7.22vs	7.37vs
6.35m	6.36m	6.34m
5.05m	5.03m	5.03m
4.69m	4.70m	4.69m
4.47m	4.48m	4.47m
4.25s	4.24s	4.23s
3.85w	3.86w	3.85w
3.66w	3.66w	3.65w
3.48vw	--	--
3.34m	3.34m	3.34m
3.16w	3.16w	3.16w
2.97w	2.94w	3.01w
2.81m	2.81m	2.80m
2.69m	2.71m	2.69m
2.14w	2.14w	2.14w
2.09m	2.09m	2.09m

ies and exposed to radiation for 24 hours. Samples were loaded without prior grinding in order to avoid the decomposition, accompanied by evolution of iodine, which had previously been observed upon grinding materials with large I/Mo ratios. The resulting patterns were quite sharp and again appeared virtually identical. Values of d calculated from the patterns are given in Table 10, from which the strong similarity between these patterns may be observed. On the basis of this similarity, it might be concluded at first that the materials having I/Mo ratios of 2.4 and 2.5 were results of contamination of a compound formulated $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{I}_3$ with iodine. However, the magnetic measurements discussed above provided strong evidence that the material formulated $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{I}_3$ is a mixed oxidation-state phase rather than a discrete compound. In light of these measurements, it seems most meaningful to postulate the existence of such a phase, homogeneous over a range of possible compositions, and to regard the iodide derivatives as different points along such a homogeneity range. Again it may be useful to consider the tentative formulation suggested above for $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{I}_3$:

By varying the values of the coefficients a , b , and c it would be possible to imagine materials having various ratios of oxidized to unoxidized dimers and various I/Mo ratios. It should

be emphasized again, however, that this formulation is used only to illustrate the presence of both oxidized and unoxidized species and does not imply knowledge of their actual composition.

In the case where a material crystallizes in such a fashion as to allow for a homogeneity range, it should theoretically be possible to see changes in the powder pattern corresponding to changes in composition. Although powder patterns arising from materials of different composition might appear very similar, changing the occupancy of sites in a lattice might be expected to cause a change in the lattice parameters, which should be detectable as a difference in d spacings. No such difference can be seen for the three materials discussed here, although this was not taken as evidence against the existence of a homogeneity range. Lines could be read out to 2θ values of only about 43° ; this may not be far enough to see measurable changes in spacing.

Given the mixed oxidation state phase, homogeneous over a range of compositions, it is of interest to consider the limits of homogeneity. No evidence was seen in the work above to infer any value for a lower limiting I/Mo ratio. Materials with I/Mo ratios near 1.5 appeared perfectly stable, and no effort was made to prepare materials with I/Mo ratios less than 1.5. However, the difficulty of preparing materials with I/Mo ratios of near 2.5, and the observed instability of such

materials with respect to loss of iodine, leads to the conclusion that the upper limiting I/Mo ratio is near 2.5.

Further studies of the benzoate system would be of interest to determine more about the nature of the oxidized species present. Of course a detailed crystal structure of one of the iodide derivatives would be interesting, although the unusual solution behavior of these materials could pose a challenge with respect to obtaining suitable crystals. It is possible that nuclear quadrupole resonance spectra might provide information about the types of iodine present in these species. However, problems could arise in preparing samples of sufficient size and in avoiding decomposition during the course of measurements. A series of magnetic susceptibility measurements conducted on materials of differing composition should reveal whether the extent of oxidation increases with increasing I/Mo ratio or whether the formation of compounds with I/Mo ratios near 2.5 represents merely an incorporation of molecular iodine into the crystal lattice.

Attempts to Reduce the Iodide Derivatives

Attempts to reduce the previously prepared $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$ were carried out in the hope that the oxidation of the carboxylate dimer could be readily reversed. It was felt that use of mild reducing agents was most likely to lead to isolation of the starting material. A hydride reducing agent was first employed; the triiodide was stirred with

$\text{Na}(\text{OC}_2\text{H}_5)(\text{OCH}_3)\text{AlH}_2$ in benzene at room temperature. The reaction was not clean; the product, a dark, tarry material, was extensively contaminated with hydride. The appearance of this product suggested that the molybdenum dimer unit had been destroyed.

Next, $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$ was heated under static vacuum in a sublimation apparatus, in the presence of zinc metal. Upon heating the apparatus to 130°C , iodine began condensing onto the cold finger, and the yellow color of $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$ could be seen below. When the system was cooled to room temperature, the iodine appeared to be reabsorbed, yielding again the $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$.

The triiodide was then heated under dynamic vacuum in the absence of zinc. Again, iodine was evolved and the formation of starting material was confirmed by an X-ray powder pattern. In light of these observations it seems that the presence of zinc did not affect the behavior of the triiodide upon heating, but that the oxidation of the carboxylates can be reversed by heating the iodide derivatives under vacuum.

Further Attempts to Oxidize the Carboxylate Dimers

Attempted Preparations of $\text{Mo}_2(\text{O}_2\text{CR})_4\text{I}$ and $\text{Mo}_2(\text{O}_2\text{CR})_4\text{I}_2$. - It

was hoped that two-electron oxidations of the carboxylates could be carried out, yielding compounds analogous to the $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$ compounds but having triple metal-to-metal bonds.

However, attempts to prepare such materials led to disturbing results. The propionate starting material, $\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4$, was reacted with iodine ($\text{I}/\text{Mo} = 1.0$) in refluxing chlorobenzene, once for two hours and once for six hours. In both cases, the intense violet color of iodine was replaced by a very deep green after thirty minutes. In both cases, yellow starting material precipitated from the solution upon cooling to room temperature. The amount of starting material appeared to be independent of reaction time. Removal of solvent from the mother liquor under high vacuum yielded only a dark green shiny material which proved to be amorphous. No iodine was lost from the material upon washing or pumping. This green product seemed clearly unrelated to the iodide derivatives prepared earlier; its amorphous nature, plus the presence of unreacted starting material, suggested a reaction in which the dimeric molybdenum unit had been destroyed.

It was also hoped that compounds of the formulation $\text{Mo}_2(\text{O}_2\text{CR})_4\text{I}$ could be prepared. These materials would be useful in that, by anion substitution, salts of colorless anions might be prepared to facilitate the recording of electronic spectra.

When $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ was reacted with iodine ($\text{I}/\text{Mo} = 0.5$) in acetonitrile, a dark solution formed but most of the starting material remained unreacted despite prolonged reaction time. The failure of this reaction to produce the desired

product might, however, have been expected on the basis of the unusual behavior of the benzoate derivatives in acetonitrile. However, the reaction was repeated twice using $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$ as the starting material and benzene and acetonitrile as the solvents. When benzene was used, a mixture of yellow starting material and red triiodide precipitated from solution. No solid products formed in acetonitrile; removal of solvent from the solution yielded a dark residue. An X-ray diffraction pattern of this residue indicated that the only crystalline materials present were $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$ and $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+ \text{I}_3^-$.

It seems evident, therefore, that formation of mono- or diiodides of these carboxylates is unfavorable with respect to formation of products richer in iodine. The unusual stability of the triiodides, in particular, is difficult to explain on the basis of the information at hand. It is possible that more detailed structural characterization of these materials will be necessary before their stability can be fully understood.

Reactions of the Carboxylates with Bromine.- The reactivities of $\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4$ and $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$ toward bromine were studied in both chlorobenzene and 1,2-dichloroethane. Formation of insoluble products was seen in all cases along with deep purple solutions. Preliminary analytical data from the insoluble materials appeared to indicate materials of stoi-

chiometry $\text{Mo}_2(\text{O}_2\text{CR})_4\text{Br}_2$; however, infrared spectra and X-ray powder measurements of all the materials suggested that none of them contained the desired dimeric structure. Infrared spectra of products differed sharply from those of the starting materials in the region of $1300\text{-}1600\text{cm}^{-1}$, indicating a possible loss of carboxylate groups. X-ray powder patterns showed that the materials were for the most part amorphous. It seems safe to conclude that the greater reactivity of bromine as compared to iodine results even under mild conditions in the formation of products unrelated to the iodide derivatives.

Reactions of the Carboxylate Dimers with Other Oxidizing

Agents.- It was hoped that salts of other anions might be prepared which would be more feasible for use in obtaining optical spectra than those containing the triiodide anion. It was hoped that a compound could be isolated in crystals of sufficient size for use in structural investigation. Accordingly, a number of reactions employing the $[\text{BF}_4]^-$ anion were studied.

When $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$ was reacted with NOBF_4 in acetonitrile, no solid products formed. Removal of solvent in vacuo yielded a mixture of starting material and a dark tar which was not characterized. When $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ was stirred with NOBF_4 in acetone, no products were isolated except for unreacted starting material. When $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ was reacted with AgBF_4 in acetone, a gray powder believed to be silver

metal precipitated from solution. The solution was filtered to remove this powder plus unreacted starting material, and solvent was removed in vacuo to yield a yellow-brown solid. An infrared spectrum of this solid differed sharply from that of the starting material and it was therefore concluded that disruption of the dimeric unit had taken place.

$\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$ was also reacted with anhydrous FeCl_3 in benzene. The solid products were a mixture of unreacted starting material and a tan solid. Although an infrared spectrum of the tan product indicated it might prove to be of interest attempts to separate it from unreacted starting material led invariably to decomposition, and the reaction was therefore abandoned.

It is not known whether oxidation of the dimer followed by rapid decomposition in solution is responsible for all of these observations, or whether the oxidizing agents employed attack at positions other than the metal-to-metal bond. Since lifetimes of the oxidized species in solution are known to be short, it seems that isolation of such species must necessitate use of oxidizing agents that not only react cleanly with the metal-to-metal bond but provide immediate stabilization of the product through precipitation.

SUMMARY

The reactivities of a group of molybdenum(II) carboxylate dimers toward various oxidizing agents were studied. Crystalline products could be isolated only by reacting the carboxylates with iodine at room temperature. Reactions of the carboxylates with $[\text{NO}]^+$, Ag^+ , Fe^{3+} and Br_2 appeared to lead to disruption of the dimeric structural unit.

The iodide derivatives were examined by elemental analysis and by a variety of physical methods in order to obtain information regarding their electronic and molecular structures. Derivatives of stoichiometry $\text{Mo}_2(\text{O}_2\text{CR})_4\text{I}_3$ could be prepared from $\text{Mo}_2(\text{O}_2\text{CC}_2\text{H}_5)_4$, $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ and $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$. In addition, derivatives with I/Mo ratios as large as 2.5 could be prepared from $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$. Infrared and electron-spin resonance measurements suggested that the materials contained singly-oxidized molybdenum dimer units. Magnetic susceptibility data for the pivalate derivative suggested that oxidation in this system was complete and pointed toward a formulation as $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$. Magnetic susceptibility data for the propionate and benzoate triiodide derivatives suggested that the benzoate in particular might be most meaningfully regarded as a mixed oxidation-state phase rather than a discrete compound. Mathematical treatments indicated that only about 65% of the molybdenum dimer units in $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{I}_3$ had been oxidized. Similar treatment of the

propionate triiodide indicated that it contained 93% oxidized dimers. X-ray diffraction patterns of benzoate derivatives having I/Mo ratios ranging from 1.5 to 2.5 were substantially identical. This observation, together with the magnetic measurements, was regarded as supporting evidence for the existence of a mixed oxidation-state phase in the benzoate system. It was felt that proportions of components in this phase varied over a homogeneity range although the limits of this range could not be stated from present information.

SUGGESTIONS FOR FURTHER WORK

Many questions remain yet unanswered about the oxidation of molybdenum(II) carboxylates. One major puzzle is the differing behavior of various carboxylates upon oxidation with iodine. It is not obvious why $\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4$ should form a product in which oxidation appears complete, while under the same conditions $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ is only 65% oxidized. There may be some hope of obtaining single-crystal data for the pivalate derivative; small crystals could be obtained by cooling saturated solutions of $[\text{Mo}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4]^+\text{I}_3^-$ in 1,2-dichloroethane. However, the anomalous behaviors of the benzoate iodide derivatives in solution, together with their apparently variable composition and tendencies toward decomposition, might lead to considerable difficulty in preparing and examining crystals. Nuclear quadrupole resonance spectra might yield information regarding the actual involvement of iodine in these systems. If samples of sufficient size could be prepared and if signals could be observed, it might be possible to detect a difference between the pivalate derivative, in which iodine is thought to be present as I_3^- , and the benzoates, which may contain both iodide and free iodine.

Electrochemical studies of the carboxylates might prove extremely fruitful. One of the unrealized goals of this research was the isolation of an oxidized dimer as the salt of an anion other than I_3^- . It was hoped that such a material

would facilitate the measurement of optical spectra as well as attempts to reverse the oxidation. It is possible that electrochemical oxidation, in the presence of a suitable anion and in an appropriate solvent system, might constitute a useful route toward the preparation of such a compound.

Further magnetic susceptibility measurements, especially of the benzoate iodides, might be of interest. By comparing moments calculated for samples having various compositions, it might be possible to study the relationship between composition and extent of oxidation in these materials. Further preparative work in this system might also serve to define the limits of homogeneity. Similar studies might be carried out on the propionate system, which appears to be intermediate in behavior between the benzoate and pivalate.

BIBLIOGRAPHY

1. R. J. Hoxmeier and R. E. McCarley, unpublished work, Iowa State University, Ames, Iowa, 1974.
2. F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson and J. S. Wood, Science, 145, 1305 (1964).
3. F. A. Cotton, Inorg. Chem., 4, 334 (1965).
4. F. A. Cotton and C. B. Harris, Inorg. Chem., 4, 330 (1965).
5. F. A. Cotton, N. F. Curtis, B. F. G. Johnson and W. R. Robinson, Inorg. Chem., 4, 326 (1965).
6. A. B. Brignole and F. A. Cotton, Inorg. Syntheses, Vol. 13, F. A. Cotton, Ed., McGraw-Hill, New York, 1972, p. 87.
7. F. Taha and G. Wilkinson, J. Chem. Soc., 5406 (1963).
8. M. J. Bennett, W. K. Bratton, F. A. Cotton and W. R. Robinson, Inorg. Chem., 7, 1570 (1968).
9. J. D. Eakins, G. D. Humphreys and C. E. Mellish, J. Chem. Soc., 6012 (1963).
10. W. K. Bratton and F. A. Cotton, J. Am. Chem. Soc., 87, 921 (1965).
11. W. K. Bratton and F. A. Cotton, Inorg. Chem., 9, 789 (1970).
12. E. Peligot, Compt. Rend., 19, 609 (1844).
13. S. Herzog and W. Kalies, Z. Anorg. Allg. Chem., 329, 83 (1964).
14. F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pipal and D. A. Ucko, J. Am. Chem. Soc., 92, 2926 (1970).
15. F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pipal and D. A. Ucko, Acta Cryst., B, 27, 1664 (1971).
16. E. Kurras and J. Otto, J. Organometal. Chem., 4, 114 (1965).
17. J. Krausse, G. Marx and G. Schödl, J. Organometal. Chem., 21, 159 (1970).

18. J. Krausse and G. Schödl, J. Organometal. Chem., 27, 59 (1971).
19. T. A. Stephenson, E. Bannister and G. Wilkinson, J. Chem. Soc., 2538 (1964).
20. D. Lawton and R. Mason, J. Am. Chem. Soc., 87, 921 (1965).
21. F. A. Cotton and J. G. Norman, Jr., J. Coord. Chem., 1, 161 (1971).
22. F. A. Cotton and J. G. Norman, Jr., J. Am. Chem. Soc., 94, 5697 (1972).
23. J. V. Brencic and F. A. Cotton, Inorg. Chem., 8, 7 (1969).
24. J. V. Brencic and F. A. Cotton, Inorg. Chem., 9, 351 (1970).
25. J. V. Brencic and F. A. Cotton, Inorg. Chem., 8, 2698 (1969).
26. J. V. Brencic and F. A. Cotton, Inorg. Chem., 9, 346 (1970).
27. J. San Filippo, Jr., Inorg. Chem., 11, 3140 (1972).
28. J. San Filippo, Jr., H. J. Sniadoch and R. L. Grayson, Inorg. Chem., 13, 2121 (1974).
29. F. A. Cotton, J. M. Troup, T. R. Webb, D. H. Williamson and G. Wilkinson, J. Am. Chem. Soc., 96, 3824 (1974).
30. F. A. Cotton and J. R. Pipal, J. Am. Chem. Soc., 93, 5441 (1971).
31. G. Albrecht and D. Stock, Z. Chem., 7, 321 (1967).
32. T. Aoki, A. Furusaki, V. Tomiie, K. Ono and K. Tamaka, Bull. Chem. Soc. Japan, 42, 545 (1969).
33. L. Ricard, P. Karagiannidis and R. Weiss, Inorg. Chem., 12, 2179 (1973).
34. A. R. Bowen and H. Taube, Inorg. Chem., 13, 2245 (1974).
35. C. L. Angell, F. A. Cotton, B. A. Frenz and T. R. Webb, J. Chem. Soc., Chem. Commun., 399 (1973).

36. F. A. Cotton, B. A. Frenz and T. R. Webb, J. Am. Chem. Soc., 95, 4431 (1973).
37. F. A. Cotton and M. Jeremic, Syn. Inorg. Metal-Org. Chem., 1, 265 (1971).
38. R. J. Hoxmeier, V. Katovic and R. E. McCarley, unpublished work, Iowa State University, Ames, Iowa, 1975.
39. C. D. Garner and R. G. Senior, J. Chem. Soc., Chem. Commun., 580 (1974).
40. F. A. Cotton and C. B. Harris, Inorg. Chem., 6, 924 (1967).
41. L. Dubicki and R. L. Martin, Aust. J. Chem., 22, 1571 (1969).
42. J. G. Norman, Jr., and H. J. Kolari, J. Chem. Soc., Chem. Commun., 303 (1974).
43. J. G. Norman, Jr. and H. J. Kolari, J. Am. Chem. Soc., 97, 33 (1974).
44. F. A. Cotton, B. A. Frenz, J. R. Ebner and R. A. Walton, J. Chem. Soc., Chem. Commun., 4 (1974).
45. E. Hochberg, P. Walks and E. H. Abbott, Inorg. Chem., 13, 1824 (1974).
46. F. A. Cotton and E. Pedersen, Inorg. Chem., 14, 383 (1975).
47. F. A. Cotton and E. Pedersen, Inorg. Chem., 14, 399 (1975).
48. J. V. Brenicic and F. A. Cotton, Inorg. Chem., 8, 1060 (1969).
49. F. A. Cotton, B. A. Frenz, E. Pedersen and T. R. Webb, Inorg. Chem., 14, 391 (1975).
50. J. G. Converse and R. E. McCarley, Inorg. Chem., 9, 1361 (1970).
51. W. K. Bratton, F. A. Cotton, M. DeBeau and R. A. Walton, J. Coord. Chem., 1, 121 (1971).
52. B. N. Figgis, Introduction to Ligand Fields, Interscience Publishers, New York, 1966.

53. J. G. Converse, Ph.D. Thesis, Iowa State University of Science and Technology, Ames, Iowa, 1968.

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