

ammonium ion,⁵ $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$, gives a stability ratio of only 250. On the other hand, if the transition state involves the combined cleavage of the remaining chelates to nickel there may not be a high positive charge from nickel on the nitrogen atom which is adjacent to the iminodiacetate group bonded to copper (or zinc) and the iminodiacetate segment serves as a better model.

The mechanism suggests (1) that EDTA type complexes with any steric hindrance to unwrapping an iminodiacetate segment will be much less readily attacked by metal ions, (2) that the rate of attack of other labile ions will parallel the stability of their iminodiacetate complexes, (3) that metal ions having slower dentate transfer (Fe^{+3} , Ni^{+2} , etc.) will be much less effective, and (4)

that factors affecting slow dentate transfer (or water loss) will affect the reaction rate. The catalysis by traces of copper ion in the zinc-nickel-EDTA reaction is indicative of a vital kinetic consideration which could spoil other exchange studies, particularly for sluggish reactions where a labile contaminant is possible. This would include radiochemical exchange studies as well as other displacement reactions. Traces of other ligands also can catalyze multi-dentate exchange reactions.⁶

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(6) D. C. Olson and D. W. Margerum, *J. Am. Chem. Soc.*, **84**, 680 (1962).

CONTRIBUTION FROM THE CLIMAX MOLYBDENUM COMPANY OF MICHIGAN RESEARCH LABORATORY, DETROIT, MICHIGAN

Synthesis and Properties of Molybdenum(III) Acetylacetonate

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Molybdenum(III) acetylacetonate, $\text{Mo}(\text{C}_5\text{H}_7\text{O}_2)_3$, was synthesized by three routes: reaction of acetylacetonone with an aqueous solution of potassium hexachloromolybdate(III), reaction of acetylacetonone with electrolytically-produced Mo^{3+} , and the reaction of $\text{Mo}(\text{CO})_6$ with refluxing acetylacetonone. It is sublimable, decomposes above its melting point (228–229°), and is monomeric in boiling benzene. Although it is non-reactive toward Lewis bases (water, benzophenone, pyridine, and triphenylphosphine), solvation in carbon tetrachloride causes replacement of one acetylacetonate group with chlorine. This new molybdenum acetylacetonate is reactive toward oxygen to yield a new, brown form of molybdenyl acetylacetonate, $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$.

Discussion

The chemistry of the acetylacetonates of molybdenum with an oxidation number of three is ill-defined. A molybdenum(III) acetylacetonate was synthesized by Morgan and Castell¹ from molybdenum oxychloride tetrahydrate, $\text{MoOCl}\cdot 4\text{H}_2\text{O}$, and acetylacetonone in aqueous alcohol. Brown crystals were obtained which analyzed as $\text{MoO}(\text{C}_5\text{H}_7\text{O}_2)\cdot 2.5\text{H}_2\text{O}$. This compound was attacked by air and was decomposed by dilute acids and alkali. The only other literature report was that of "molybdenum(III) acetylacetonate" in a report of some cell constants and paramagnetic resonance.^{2,3}

The only well established molybdenum acet. I-acetonate is the yellow molybdenyl acetylacetonate, $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$, which is a derivative of the

MoO_2^{2+} cation. Unfortunately, this molybdenum(VI) acetylacetonate has limited solubility and is readily decomposed in solution.⁴ It was deemed advisable to attempt the synthesis of a hexacoöordinate molybdenum(III) acetylacetonate because Mo^{3+} would have an ideal d^3 configuration for a stable octahedral structure, as predicted by the ligand-field theory.⁵ It also was hoped that this molybdenum(III) chelate

(1) G. T. Morgan and R. A. S. Castell, *J. Chem. Soc.*, 3252 (1928).

(2) H. S. Jarrett, *J. Chem. Phys.*, **27**, 1298 (1957).

(3) A recent private communication from Dr. J. C. Thomas, E. I. du Pont de Nemours and Company, reveals an independent synthesis of this compound by an electrolytic process.

(4) W. C. Fernelius, K. Terada, and B. E. Bryant, *Inorg. Syn.*, **6**, 147 (1960).

(5) L. E. Orgel, "An Introduction to Transition-Metal Chemistry: Ligand-Field Theory," John Wiley & Sons, Inc., New York, N. Y., 1960.

would possess the outstanding organic solubility and volatility characteristics of transition metal acetylacetonates.

It was found that potassium hexachloromolybdate(III), K_3MoCl_6 , a molybdenum(III) species known to possess considerable air and hydrolytic stability, would react with excess acetylacetonone in aqueous solution to give a good yield of molybdenum(III) acetylacetonate, $Mo(C_5H_7O_2)_3$. It also could be obtained using the Mo^{3+} cation, formed by the electrolytic reduction of the molybdate anion in aqueous hydrochloric acid. Furthermore, it was found possible to synthesize the same compound by complete displacement of carbon monoxide from molybdenum hexacarbonyl in refluxing acetylacetonone. This is the first reported instance of an organic ligand accomplishing such a reaction with molybdenum hexacarbonyl.⁶

Molybdenum(III) acetylacetonate [tris-(2,4-pentanedione)-molybdenum(III)] is a dark purple, crystalline solid, m.p. 228–229°. Because of its reactivity toward oxygen, it must be synthesized and characterized in an inert atmosphere. The attack of molecular oxygen gives a new, brown form of molybdenyl acetylacetonate, $MoO_2(C_5H_7O_2)_2$, m.p. 284–285°. Molybdenum(III) acetylacetonate decomposes above its melting point to lose one acetylacetonate group. Acetylacetonone is a major decomposition product for both oxidative and thermal decomposition. The molybdenum(III) acetylacetonate can be vacuum sublimed without decomposition, and it is readily soluble in benzene, in which it is monomeric. It is soluble in carbon tetrachloride, but refluxing of this solution causes decomposition with replacement of acetylacetonone by chlorine. Although molybdenum(III) acetylacetonate is soluble in benzophenone, pyridine, and triphenylphosphine, the complex does not react with these solvents at elevated temperatures and it is insoluble in and unattacked by boiling water. These properties suggest that the bidentate chelated, hexacoordinated molybdenum(III) is quite stable toward Lewis bases, but is subject to attack by free radical systems.

Experimental

The experiments were performed under a prepurified nitrogen atmosphere. All material transfers of unstable materials were conducted in a nitrogen controlled-atmosphere glove box. Deaerated, distilled water was employed

as both the reaction medium and the wash solvent for the aqueous syntheses. The low oxygen content of the nitrogen atmosphere was checked by gas chromatography, using a Molecular Sieve column. The infrared spectra were determined using a Perkin-Elmer Corporation Model 21 instrument, and samples were prepared as potassium bromide disks and Nujol mulls. All melting points are corrected.

Materials.—The potassium hexachloromolybdate(III), a commercial product, was found to be free of water and hydroxide by infrared spectroscopy.

Anal. Calcd. for K_3MoCl_6 : K, 27.53; Mo, 22.52; Cl, 49.94. Found: K, 27.69; Mo, 22.48; Cl, 50.13.

The molybdenum trichloride and molybdenum hexacarbonyl were products of Climax Molybdenum Company. Acetylacetonone (2,4-pentanedione) and *o*-xylene were Eastman White Label grade. Dibenzoylmethane was also Eastman White Label and was found to have the reported infrared spectrum.⁷ Benzophenone was Matheson Coleman & Bell reagent grade. Carbon tetrachloride and pyridine were Baker reagents.

Reaction of Potassium Hexachloromolybdate(III) with Acetylacetonone in Aqueous Solution.—Fifty ml. (48.8 g., 0.49 mole) of acetylacetonone was dissolved in 500 ml. of water at 50°. After slight cooling, 20.0 g. (0.048 mole) of potassium hexachloromolybdate(III) was added, and complete solution was obtained after stirring for a short time. This solution was heated gradually to 50° over a 20-min. period and maintained at 50–55° for 1 hr. During this period a considerable amount of dark purple, crystalline solid formed. The crystals were separated by vacuum filtration and washed with water. This product was vacuum (oil pump) dried while heating gently with an infrared lamp. The dark purple crystals, m.p. 228–229°, weighed 16.7 g. (89% yield based on the K_3MoCl_6 used).

Anal. Calcd. for $C_{15}H_{21}MoO_6$: C, 45.81; H, 5.38; Mo, 24.40. Found: C, 46.12; H, 5.65; Mo, 24.30. The molecular weight, determined ebullioscopically in benzene, was 393; calculated: 393.27.

Potassium bromide disks and Nujol mulls⁸ were prepared in a nitrogen atmosphere and used in a sealed cell to obtain the infrared absorption spectra. The following peaks, very similar to those described for acetylacetonates of trivalent metal ions,⁹ were obtained in the 1650–750-cm.⁻¹ region: 1550 s,sh; 1527 s; 1429 m; 1370 s; 1274 s; 1193 w; 1020 m; 930 m; 778 m (s, strong; sh, shoulder; m, medium; w, weak absorption).

Electrolytic Synthesis of Molybdenum(III) Acetylacetonate.—An aqueous solution of Mo^{3+} was prepared by the electrolytic reduction of a solution containing 45 g. of ammonium paramolybdate (0.256 g.-atom of molybdenum) in 150 ml. of 8 *N* hydrochloric acid. The electrolysis apparatus consisted of a mercury pool cathode and a carbon rod anode in an unglazed alundum cup. The anolyte was concentrated hydrochloric acid.

A total of 28.1 amp-hr. (37% excess of theoretical) was employed while maintaining a cathode current density of 0.041–0.055 amp./cm.². To the resulting dark, reddish brown solution was added 34.1 g. (0.34 mole) of acetyl-

(7) L. Sacconi, G. Caroti, and P. Paoletti, *J. Inorg. Nucl. Chem.*, **8**, 93 (1958).

(8) There was no observable interaction with the sample medium

(9) K. E. Lawson, *Spectrochim. Acta*, **17**, 248 (1961).

(6) J. Chatt, P. L. Pauson, and L. M. Venanzi, "Organometallic Chemistry," Reinhold Publ. Corp., New York, N. Y., 1960, p. 482.

acetone. The stirred reaction mixture was neutralized (pH 6–7) by the slow addition of aqueous ammonia. The reaction mixture then was heated to 50° over a 30-min. period and maintained at this temperature for 45 min. A reddish solid formed which was separated by filtration and was washed with water. The crude solid product was vacuum sublimed (0.07 mm., 170–180°) for 11.5 hr. to obtain 11.7 g. (11.7% yield based upon molybdenum) of dark, red-purple sublimate, m.p. 223–225°. The infrared spectrum of this product is essentially identical with that of the product derived from potassium hexachloromolybdate(III).

The low yield from this synthesis is explained by the lack of sufficient acetylacetone. Previous syntheses employing potassium hexachloromolybdate(III) have demonstrated that at least a 100% molecular equivalent excess is necessary for high yield. In this experiment only 1.3 molecular equivalents were employed, whereas the reaction stoichiometry requires three molecular equivalents. Despite this error, an appreciable yield of product was obtained, which demonstrates the ease of formation of the triacetylacetonate from the Mo^{3+} cation in aqueous solution.

Reaction of Molybdenum Hexacarbonyl with Acetylacetone as Solvent.—A stirred reaction mixture containing 19.47 g. (0.0738 mole) of molybdenum hexacarbonyl and 100.0 ml. (97.53 g., 0.975 mole) of acetylacetone was heated in a nitrogen atmosphere to a temperature of 150° over a 1.5-hr. period. The bath temperature was maintained at 150–155° for 6 hr.; the molybdenum carbonyl which sublimed from the mixture was returned at intervals to the reaction flask. After 6 hr. no more molybdenum carbonyl sublimed. The reaction mixture then was vacuum (oil pump) evaporated to dryness while gradually heating to 96°. The cooled reaction flask then was equipped with an air-cooled cold finger for vacuum (oil pump) sublimation. The reaction mixture was sublimed for 7–8 hr. at a bath temperature of 170–180°. The sublimate consisted of 27.08 g. (93% yield) of dark purple crystals, m.p. 225–226°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{21}\text{MoO}_6$: C, 45.81; H, 5.38; Mo, 24.30. Found: C, 44.87; H, 5.25; Mo, 23.80.

The infrared spectrum of this product is essentially identical with that of the product prepared from potassium hexachloromolybdate(III). A further proof of this identity is the mixed melting point of 227–229°.

The condensate, largely acetylacetone, from the vacuum evaporation of the reaction mixture was fractionally distilled to obtain a dark brown liquid residue, 2.03 g., n_D^{20} 1.4875, which did not distil up to a pot temperature of 210°. This complex organic by-product, which may be a result of the oxidation of the molybdenum(0) by acetylacetone, was not further investigated.

The competitive power of aromatic coordination bonding relative to acetylacetone chelate bonding was studied. An *o*-xylene solution of molybdenum hexacarbonyl and acetylacetone was refluxed for 9 hr. Since air oxidation of the reaction mixture yielded only the brown molybdenyl acetylacetonate, it can be concluded that there was no formation of *o*-xylene molybdenum tricarbonyl.

Air Oxidation of Molybdenum(III) Acetylacetonate.—Molybdenum(III) acetylacetonate, $\text{Mo}(\text{C}_5\text{H}_7\text{O}_2)_3$, was attacked by atmospheric oxygen to yield a brown molyb-

denyl acetylacetonate [bis-(2,4-pentanediono)-dioxomolybdenum(VI)], $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$, m.p. 284–285°. On some occasions air oxidation was quite rapid, producing considerable heat, smoke, and red glow spots. Controlled, stepwise reaction with pure oxygen demonstrated that acetylacetone was a major organic product. The crude molybdenyl acetylacetonate could only be purified by repeated crystallization from acetylacetone solution.

Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{MoO}_8$: C, 36.82; H, 4.33; Mo, 29.43. Found: C, 37.77; H, 4.63; Mo, 29.13.

Attempted crystallization from benzene and chloroform indicated decomposition by the boiling solvents. The brown molybdenyl acetylacetonate is insoluble in water, ethanol, tetrahydrofuran, diethyl ether, and carbon tetrachloride at room temperature. It dissolves in chloroform, methylene chloride, and *p*-dioxane. Upon warming with tetrahydrofuran, a brown solution was obtained which rapidly turned blue. The blue color suggests that the molybdenum is being reduced to Mo^{6+} .

The brown $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ is a more stable isomer of the unstable yellow form, m.p. 185°. The unstable isomer is readily decomposed by most organic solvents, is hydrolytically unstable, and is readily subject to ultraviolet promoted oxidation–reduction in the presence of water. An unsuccessful attempt was made to convert this unstable isomer to the higher melting brown form by slow heating in a nitrogen atmosphere (maximum temperature 193°). Only a yellow sublimate of the unstable isomer was obtained, as well as a dark, chloroform-insoluble residue.

The infrared spectrum of the brown molybdenyl acetylacetonate has a strong band at about 960 cm^{-1} which is assigned to the $\text{Mo}=\text{O}$ stretching frequency.¹⁰ This band is absent in the spectrum of the less chemically stable yellow isomer, but a strong band appears at 935 cm^{-1} . This absorption at lower frequency probably is analogous to that found in the infrared spectrum of molybdenum trioxide and suggests that the molybdenyl group of the yellow isomer has less double band character than the brown compound. The low frequency absorptions of molybdenum trioxide have been attributed to $\text{Mo}-\text{O}-\text{Mo}$ groupings and the higher frequency absorption to $\text{Mo}=\text{O}$.¹⁰ It is proposed that the molybdenyl oxygens of the yellow isomer are associated with adjacent molybdenum atoms in the crystalline state. It is significant that MoO_2Cl_2 , an efficient source of the MoO_2^{2+} cation for the synthesis of the yellow $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$,¹¹ also lacks strong absorption at about 960 cm^{-1} and shows strong bands at lower frequencies.¹²

Molybdenum hexacarbonyl was treated with molten dibenzoylmethane (1,3-diphenyl-1,3-propanedione) at 140°. The reaction mixture was dissolved in benzene, and air was introduced to obtain black crystals, m.p. 298–300°, which correspond approximately to $\text{MoO}_2\text{--}[(\text{C}_6\text{H}_5\text{CO})_2\text{CH}]_2$, bis-(1,3-diphenyl-1,3-propanediono)-dioxomolybdenum(VI). The infrared spectrum was found to be essentially identical with that of the known uranyl analog,⁷ except for the 885 to 1000 cm^{-1} region, which distinguishes differences in metal–oxygen bonding.¹⁰

(10) C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 3552 (1959).

(11) M. L. Larson, unpublished work.

(12) A paper on the chemical and physical properties of molybdenyl acetylacetonates is forthcoming.

It is significant that, similarly to the molybdenyl acetylacetonate isomers, a lower melting isomer, m.p. 112°, was synthesized by the inefficient condensation reaction of molybdic oxide with dibenzoylmethane.¹

Reaction of Molybdenum(III) Acetylacetonate with Carbon Tetrachloride.—A solution of 1.23 g. (3.13 mmoles) of molybdenum(III) acetylacetonate in 50 ml. of carbon tetrachloride was refluxed for 2 hr. Upon standing at room temperature, 0.10 g. of an orange-brown solid, m.p. 155–160°, was separated from the reaction mixture by filtration. The filtrate was vacuum evaporated to obtain a mixed solid. This was extracted with carbon tetrachloride to obtain 0.36 g. of a brown, insoluble solid, m.p. 161–163°.

Anal. Found: C, 35.93; H, 4.12; Cl, 11.80; Mo, 27.72. The composition of this solid corresponds to an empirical formula of $C_{10.3}H_{14.1}Cl_{1.14}MoO_{4.41}$. The infrared spectrum showed no lines in the region 700–750 cm^{-1} , normally attributed to C–Cl bonding, and dissolution with hot water gave chloride anion. These data suggest that the product is essentially a molybdenum chloride diacetylacetonate.

The reaction was re-examined using a 9-hr. reflux period. A solid, similar to that isolated in the previous reaction, was isolated, but its infrared spectrum showed C–Cl bonding and it contained more chlorine.

Anal. Found: C, 28.04; H, 3.04; Cl, 27.98; Mo, 25.06. The analysis corresponds to an empirical formula of $C_{8.98}H_{11.6}Cl_{3.04}MoO_{3.82}$. These results indicate that the reaction with carbon tetrachloride is non-specific and yields products of variable composition.

Reactions of Molybdenum(III) Acetylacetonate with Lewis Bases.—A series of Lewis base solvents were examined with results as given below.

Water.—A mixture of molybdenum(III) acetylacetonate and deaerated water was heated at reflux for 1 hr. Water was removed by vacuum evaporation to obtain dark purple crystals, m.p. 225–227°, whose infrared spectrum corresponded to the starting material.

Benzophenone.—A solution of molybdenum(III) acetylacetonate in molten benzophenone was heated to 153° and vacuum distilled up to a maximum bath temperature

of 184°. Greater than 99% of the benzophenone was recovered, and greater than 90% of the unreacted molybdenum(III) acetylacetonate was recovered either as a pure vacuum sublimate or as the oxidation product, the brown molybdenyl acetylacetonate.

Pyridine.—A solution of molybdenum(III) acetylacetonate in this solvent was heated at reflux for 2 hr. After removal of the pyridine by vacuum evaporation, the starting material was vacuum sublimed unchanged from the residue.

Triphenylphosphine.—A solution of molybdenum(III) acetylacetonate in molten triphenylphosphine was heated at 108–110° for 3 hr. The reaction mixture was dissolved in benzene, and air was passed through the solution to isolate the starting material as the oxidation product, molybdenyl acetylacetonate.

Reaction of Molybdenum Trichloride with Refluxing Acetylacetone.—An early attempt at the synthesis of a molybdenum(III) acetylacetonate was the reaction of a suspension of molybdenum trichloride with refluxing acetylacetone. The non-solvent reaction mixture was refluxed for 17.5 hr. From this reaction mixture was filtered 71.5% of the starting molybdenum trichloride and a 29.4% yield of the crude, brown molybdenyl acetylacetonate. An unidentified, colorless organic condensation product (m.p. 176–178°), with an analysis corresponding to the formula $C_{6.35}H_{8.65}O_{1.00}$, also was isolated.

Apparently the reaction fails because of the high lattice energy and polymeric nature of molybdenum trichloride.

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