

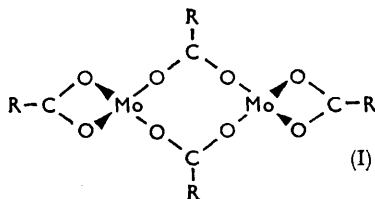
487. *Molybdenum(II) Carboxylates.*

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A number of molybdenum(II) carboxylates have been obtained by the interaction of mono- and di-carboxylic acids with hexacarbonylmolybdenum. The monocarboxylates appear to have a dimeric structure involving both bridging and chelating carboxylate groups. The corresponding benzenesulphonate and diphenylphosphinate are reported.

*Monocarboxylates of Molybdenum(II).*—The compounds of stoichiometry  $\text{Mo}(\text{O}\cdot\text{COR})_2$  (where  $\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{Pr}^i, \text{C}_6\text{H}_{11}, \text{C}_7\text{H}_{15}, \text{C}_3\text{F}_7, \text{C}_6\text{H}_5, m\text{-C}_6\text{H}_4\text{Me}, \text{C}_6\text{H}_4\text{OH}, \text{and } \text{C}_6\text{H}_4\text{F}$ ) have been prepared; the acetate<sup>1</sup> and benzoate<sup>2</sup> have been briefly described previously. Hexacarbonylmolybdenum was heated, either alone or in diethyleneglycol dimethyl ether (diglyme), with the carboxylic acid together with a small amount of its anhydride if available. The compounds are all yellow solids and some of them form very fine needle-like crystals. They are thermally quite stable, and the alkyl carboxylates can be sublimed unchanged in a vacuum at temperatures exceeding 300°. The solubility depends on the nature of the carboxylate group but the lower alkyl carboxylates are insoluble in hydrocarbon and halogenated solvents; they are sparingly to moderately soluble in acetone or tetrahydrofuran but the solutions turn brown and eventually blue on exposure to air.

Although a polymeric structure involving tetrahedral molybdenum(II) and bridging acetate groups is a possibility,<sup>1</sup> and would be in keeping with the low solubility of the compounds, they appear to be dimeric with both bridging and chelating carboxylate groups and tetrahedrally co-ordinated molybdenum(II). Evidence for the dimeric structure is two-fold. First, the perfluorobutyrate is sufficiently soluble (and the solutions sufficiently air-stable) in cold acetone, cold benzene, and boiling toluene to allow the molecular weight to be determined by both osmometric and ebullioscopic methods. The salicylate is also dimeric in cold acetone (osmometric method). Conductivity measurements on solutions of the perfluorobutyrate in acetone and nitrobenzene and of aryl carboxylates in acetone show that the solutions are non-conducting, *e.g.*, for the perfluorobutyrate in acetone  $\Lambda_{0.001\text{M}} = 4.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ .



Secondly, a single-crystal *X*-ray-diffraction study of molybdenum(II) acetate<sup>3</sup> is sufficiently advanced to substantiate the dimeric geometry of the molecule. All the carboxylates are diamagnetic, and this is consistent with tetrahedral co-ordination by oxygen for a  $d^4$  configuration of molybdenum(II), as in (I).

*Infrared Spectra.*—It is well known that there are no reliable infrared criteria for distinguishing between chelating and bridging carboxylate groups, and even in the present compounds, where it is clear that for the first time both types of group are present on the same metal atom, there is no obvious splitting of the symmetric and asymmetric carboxylate stretching frequencies (Table 1). The assignment of the asymmetric stretch in the aryl carboxylates is complicated by a strong band at 1525—1475  $\text{cm}^{-1}$  due to skeletal in-plane vibrations.<sup>4</sup> However, all the carboxylates have strong bands in the region where bridging carboxylate groups are known to absorb, as in chromium(II), copper(II), and

<sup>1</sup> Bannister and Wilkinson, *Chem. and Ind.*, 1960, 319.

<sup>2</sup> Abel, Singh, and Wilkinson, *J.*, 1959, 3097.

<sup>3</sup> Lawton and Mason, personal communication.

<sup>4</sup> Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, 2nd edn., p. 64.

basic beryllium acetate,<sup>5</sup> or in the rhenium,<sup>6</sup> rhodium,<sup>7,8</sup> palladium,<sup>8</sup> and ruthenium<sup>8</sup> carboxylates. The alkyl carboxylates have a splitting of the asymmetric stretching frequency of *ca.* 8—18 cm.<sup>-1</sup>. This splitting can be attributed either to a slight difference

TABLE I.

Infrared spectra (carboxylate bands) (in cm.<sup>-1</sup>) of molybdenum(II) monocarboxylates.

Compound *	Asym. stretch	Sym. stretch	Asym. deform.
Acetate .....	1512s, 1494s †	1409s	675s
n-Butyrate .....	1502vs, 1494vs	1425vs	671m
Isobutyrate .....	1502vs, 1489vs	1422vs	672m
Cyclohexane carboxylate .....	1498s	1423s	—
Perfluorobutyrate .....	1584s ††	1427m	—
Benzoate <sup>2</sup> .....	1494s, 1477m †	1404s	677m
Fluorobenzoate .....	1506s, 1495s	1407s	—
Salicylate .....	1507m, 1484s	1384s	670s
m-Toluate .....	1504vs, 1483s	1395vs	673s

\* All as yellow needles. † In mulls on Grubb-Parsons Spectromaster grating instrument; values to  $\pm 0.5$  cm. ‡ In benzene, 1600 cm.<sup>-1</sup> (sharp).

in the force constants for the chelating and bridging carboxylate groups or to solid-state interactions within the lattice. The insolubility or instability of alkyl carboxylates in suitable organic solvents prevents the examination of solution spectra; although some of the aryl carboxylates are soluble without decomposition for short periods in acetone, chloroform, or methanol, these solvents are not satisfactory in the 1500—1450 cm.<sup>-1</sup> region. Only the perfluorobutyrate can be studied in both benzene solution and in the solid state, and here there is no splitting at all, even with the grating instrument. It seems reasonable, therefore, to conclude that there is little if any difference between the spectra of chelating and bridging carboxylate groups, and that any small differences observed in solid-state spectra are equally well attributed to crystal effects.

*Chemical Properties.*—The carboxylates appear to be stable indefinitely in the absence of air. On exposure to moist air, molybdenum(II) acetate turned green over a period of weeks and after some months became dark blue, losing acetic acid. The blue material has a strong infrared band at 940—970 cm.<sup>-1</sup>, and appears to be “molybdenum blue.” The higher alkyl carboxylates are rather more sensitive to moist air than is the acetate. The perfluorobutyrate is more stable, and even when exposed to air for over a year showed little sign of decomposition other than a green coating on the crystals. The compound is soluble in ethanol, methanol, dichloromethane, benzene, and toluene, the solutions being insensitive to air for periods of several hours. The aryl carboxylates are also fairly stable in the solid state in air, but their solutions in organic solvents decompose within 30 minutes.

The acetate reacts with dry hydrogen chloride at temperatures above *ca.* 130°, a brown material being obtained. The dark brown product from the reaction at *ca.* 250° analyses approximately as molybdenum dichloride (*ca.* 98% MoCl<sub>2</sub>), but we have never been able to obtain a material entirely free from carbon, hydrogen, or oxygen. The substance is clearly not the usual yellow “molybdenum dichloride,” Mo<sub>6</sub>Cl<sub>12</sub>. It has some reactions which could be expected of the true dichloride. Thus it dissolves, leaving a small residue, however, in hot pyridine and hot isoquinoline to give very air-sensitive yellow and blood-red solutions, respectively. The solid is stable in air, and is insoluble in, and unaffected by, water and concentrated hydrochloric acid.

The acetate and other alkyl carboxylates react with triphenylphosphine, pyridine, piperidine, and other donor ligands. The adducts are often insoluble, and are all air- and

<sup>5</sup> For discussion and references see Nakamoto, “Infrared Spectra of Inorganic and Coordination Compounds,” Wiley, New York and London, 1963, pp. 197 *et seq.*

<sup>6</sup> Taha and Wilkinson, *J.*, 1963, 5406.

<sup>7</sup> Johnson, Hunt, and Neumann, *Inorg. Chem.*, 1963, 2, 960.

<sup>8</sup> Morehouse, Powell, Stephenson, and Wilkinson, unpublished work.

moisture-sensitive and impossible to purify. However, the acetate is soluble in pyridine from which yellow crystals can be obtained; these are diamagnetic, have the empirical formula  $\text{Mo}(\text{O}\cdot\text{COMe})_2\cdot\text{py}$ , and have an infrared spectrum showing strong carboxylate bands at 1410 and 1500  $\text{cm}^{-1}$ , as well as characteristic pyridine bands.<sup>9</sup> We have been unable to determine the molecular weight but it seems reasonable to assume that pyridine has merely added to the dimeric acetate to give a pentaco-ordinate molybdenum(II) complex. A similar benzoate complex can also be obtained. Both compounds are air-sensitive, the solutions in pyridine turning red. When a solution of the acetate in pyridine is allowed to stand in moist air, a reddish-brown powder is deposited. This is completely insoluble in all common organic solvents except dimethyl sulphoxide and dimethylformamide, which give deep yellow solutions, and, to a very limited extent, nitrobenzene and nitromethane. The infrared spectrum of this material shows evidence for pyridine, but no water, OH, pyridinium, or acetate bands. Analyses correspond closely to an empirical formula  $\text{MoO}_4\cdot\text{py}$ . A material of very similar analysis and identical spectroscopic properties can be obtained by addition of pyridine to an ethanolic solution of molybdenum oxotrichloride. In both materials, a simple band at *ca.* 950  $\text{cm}^{-1}$  can be assigned to Mo=O stretching. It seems likely that the other oxygen atoms are present as oxo-bridges in a highly polymeric structure.

*Dicarboxylates of Molybdenum(II).*—The interaction of hexacarbonylmolybdenum with dicarboxylic acids under strictly anhydrous conditions gives green powders of composition  $\text{Mo}(\text{O}\cdot\text{CO}\cdot[\text{CH}_2]_n\cdot\text{CO}\cdot\text{O})$ , where  $n = 3$  or 4, while, in the presence of small amounts of water, green hydrates,  $\text{Mo}(\text{O}\cdot\text{CO}\cdot[\text{CH}_2]_n\cdot\text{CO}\cdot\text{O})\text{H}_2\text{O}$ , are obtained for  $n = 2, 3$ , or 4. The substances are quite insoluble in organic solvents like acetone or alcohol, but they dissolve in warm dimethylformamide or dimethyl sulphoxide giving greenish-yellow solutions which decompose quite rapidly. The solids are also quite unstable, turning brown after *ca.* 15 minutes, although the succinate remained green for several days and its hydrate for about an hour. The infrared spectra of the anhydrous and hydrated compounds are similar except for bands due to water in the latter compound (at 3300m and *ca.* 1650w  $\text{cm}^{-1}$ ). Strong bands in the 1400—1500  $\text{cm}^{-1}$  region are due to asymmetric and symmetric carboxylate stretches, while an additional broad band at 1700—1725  $\text{cm}^{-1}$  is probably due to the unco-ordinated carboxylate group.

#### EXPERIMENTAL

Microanalyses and molecular weights were by the Microanalytical Laboratory, Imperial College. Infrared spectra were taken on Perkin-Elmer model 21 and Grubb-Parsons Spectromaster grating instruments, using Nujol and hexachlorobutadiene mulls. Magnetic measurements were made by the standard Gouy method. Molybdenum was determined by ignition to molybdenum trioxide at 500—525°, or gravimetrically as the oxinate.

All preparations were carried out under nitrogen. Analytical data are collected in Table 2.

*Monocarboxylates.*—(1) For the acetate, propionate, butyrates, and perfluorobutyrate, an excess of acid, together with a small amount of its anhydride where available, and hexacarbonylmolybdenum (*ca.* 2 g.) were heated under reflux (below 150°) until gas evolution ceased.

(2) For all other acids, the hexacarbonyl and the acid (in a 1 : 2.2 mole ratio) were dissolved in the minimum amount of diglyme (dried by molecular sieves and freshly distilled) and heated at *ca.* 150° until gas evolution ceased.

For the acetate, benzoate, *p*-fluorobenzoate, and cyclohexane carboxylate, yellow crystals separated during the reaction. The crystals were collected, washed with warm alcohol, then anhydrous ether, and dried *in vacuo*. In other cases, the reaction mixture was cooled to 0° for several hours, after which the crystals were collected, washed several times with light petroleum (b. p. 60—80°), and dried *in vacuo* at 130°. The perfluorobutyrate was recrystallised from hot toluene. For the octanoate, the diglyme was removed *in vacuo* and the residue thoroughly extracted with ether and dried.

<sup>9</sup> See Gill, Nuttall, Scaife, and Sharp, *J. Inorg. Nuclear Chem.*, 1961, **18**, 79.

TABLE 2.  
Analyses of molybdenum(II) carboxylates and related compounds.

Compound	Formula	Found (%)				Required (%)			
		C	H	O	Mo	C	H	O	Mo
Acetate	$C_4H_8MoO_4$	22.6	2.9	29.8	45.0	22.4	2.8	29.4	44.8
Propionate	$C_6H_{10}MoO_4$	29.6	4.1	26.2	39.5	29.8	4.2	26.4	39.6
n-Butyrate	$C_8H_{14}MoO_4$	35.7	5.2	—	—	35.6	5.2	—	—
Isobutyrate	$C_8H_{14}MoO_4$	35.7	5.2	—	—	35.6	5.2	—	—
Cyclohexane carboxylate	$C_{12}H_{22}MoO_4$	48.1	6.5	18.4	27.2	48.0	6.3	18.3	27.4
Octanoate	$C_{16}H_{30}MoO_4$	49.5	7.9	—	—	50.3	7.9	—	—
Perfluorobutyrate	$C_4F_8MoO_4$	18.9	—	—	18.2	18.4	—	—	18.4
Fluorobenzoate*	$C_{14}H_8F_2MoO_4$	45.1	2.3	—	25.7	45.0	2.1	—	25.6
Salicylate	$C_{14}H_{10}MoO_6$	46.0	3.4	—	—	45.2	3.2	—	—
m-Toluate	$C_{16}H_{14}MoO_4$	51.6	3.9	17.0	—	52.2	4.3	17.4	—
Benzenesulphonate	$C_{12}H_{10}MoO_6S_2$	36.0	2.8	22.8	23.4	35.1	2.5	23.4	23.4
Diphenylphosphinate	$C_{24}H_{20}MoO_4P_2$	54.2	4.0	—	17.9	54.4	3.8	—	18.1
Succinate	$C_4H_4MoO_4$	22.9	2.2	—	45.7	22.5	1.9	—	45.3
Succinate hydrate	$C_4H_6MoO_5$	20.8	2.6	—	42.8	20.9	2.6	—	42.8
Adipate	$C_6H_6MoO_4$	29.0	3.7	25.3	—	29.9	3.3	26.5	—
Adipate hydrate	$C_6H_{10}MoO_5$	—	—	—	37.2	—	—	—	37.3
Gluterate hydrate	$C_5H_8MoO_5$	24.1	3.2	—	39.5	24.6	3.2	—	39.3

\* Found: F, 10.3.  $C_{14}H_8F_2MoO_4$  requires F, 10.2%.

In addition to the data given in Table 1, the carboxylates had the bands expected from the aliphatic or aromatic groups present. For the perfluorobutyrate (requires *M*, 1044): found by Mechrolab Osmometer (at 37°) in acetone, 1025; in benzene, 1020; by ebullioscopy in toluene, 1020. For the salicylate (requires *M*, 744): found by osmometer in acetone, 720.

*Dicarboxylates*.—Method (2) was used in all cases, but with an excess (*ca.* 10%) of hexacarbonylmolybdenum. When the solid dicarboxylate began to separate from the diglyme reaction mixture, the heating was stopped and the mixture was cooled to 0°. The green precipitate was collected, washed with acetone and anhydrous ether, and analysed immediately. When the diglyme and the apparatus were not specially dehydrated, the product was the hydrated dicarboxylate. The anhydrous complexes were obtained only under strictly anhydrous conditions and using diglyme distilled over sodium directly into the reaction flask.

The diphenylphosphinate, which is assumed to be similar to the carboxylates but with OCO replaced by OPO, was obtained by method (2) as a salmon-pink powder; it was washed thoroughly with ether and dried *in vacuo*. Similarly, interaction with benzenesulphonic acid gave a greenish-grey powder. The analytical results are given in Table 2.

*Pyridine Adducts*.—(1) To molybdenum acetate or benzoate (*ca.* 2 g.) was added, in a nitrogen atmosphere, excess of pyridine (dried, redistilled, and deoxygenated) (*ca.* 5 ml.); after warming to dissolve the crystals, the yellow solution was allowed to cool and the large yellow plate-like crystals were collected, rinsed with pyridine and then ether, and, after being dried *in vacuo* (*ca.* 15 min.), were analysed immediately. The *acetate*, m. p. 130–140° (decomp.) (Found: C, 37.2; H, 3.8; N, 4.6; Mo, 34.3.  $C_9H_{11}NMoO_4$  requires C, 36.8; H, 4.1; N, 4.8; Mo, 32.7%), and the *benzoate* (Found: C, 54.4; H, 4.1; N, 3.4; Mo, 25.4.  $C_{19}H_{15}NMoO_4$  requires C, 54.6; H, 3.6; N, 3.4; Mo, 23.0%) were prepared.

(2) A warmed solution of the acetate (2 g.) in pyridine was filtered and allowed to stand in air for *ca.* 12 hr. The red, semicrystalline powder was collected, washed several times with pyridine, then light petroleum (b. p. 60–80°), and dried *in vacuo* at 80° for several hours (yield *ca.* 0.5 g.) (Found: C, 24.1; H, 2.3; N, 5.6; Mo, 42.3.  $C_5H_5NMoO_4$  requires C, 25.1; H, 2.1; N, 5.8; Mo, 40.2%).

We thank the Climax Molybdenum Company for gifts of hexacarbonylmolybdenum.

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[Received, November 30th, 1963.]