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Preparation and Characterization of Some Dimolybdenum(II) Carboxylates[1a]

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The reaction of $Mo_2X_4L_4$ [L = $(n\text{-}C_4H_9)_3P$] with benzoic acid produces either $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2X_2$, $(C_6H_5CO_2)_4Mo_2{\cdot}2P(n\text{-}C_4H_9)_3$, or $(C_6H_5CO_2)_4Mo_2$ depending on reaction conditions. Under similar conditions, alkylcarboxylic acids yield only the corresponding tetrakis-μ-(carboxylato) complex, $(RCO_2)_4Mo_2$. The near-uv–visible spectra of the tetrakis-μ-(arylcarboxylato) complexes are characterized by an intense, broad band, the position of which varies substantially with solvent donor nature. Spectral data indicate that the π framework of the aryl rings in these complexes is conjugated with the metal–metal chromophore. In addition, resonance Raman studies indicate that the intense, characteristic transition in the optical spectrum of $(4\text{-}NCC_6H_4CO_2)_4Mo_2$ (and presumably other tetrakis-μ-(arylcarboxylate) complexes of Mo_2^{4+}) involves significant and probably simultaneous change in the occupancy of both the metal–metal and the carboxylate orbitals, suggesting the involvement of a common molecular orbital. The chemical, spectroscopic, and structural relationships that exist between those complexes are discussed.

Introduction

The structural diversity and chemical reactivity of dinuclear complexes with strong metal-to-metal bonds have made them the focus of considerable current interest.[2] Such bonds are particularly prodigious in the chemistry of molybdenum(II). In an effort to determine the range of chemical reactivity of these complexes, we have undertaken an examination of their ligand substitution and redox behavior. Here, we report the preparation and characterization of a series of dinuclear molybdenum(II) carboxylates and the chemical, spectroscopic, and structural relationships that exist between them.

Experimental Section

Materials. Carboxylic acids and tri-*n*-butylphosphine were obtained commercially. The former were used without further purification; the latter was distilled under reduced pressure prior to use. All solvents were purchased as spectral quality or were purified according to standard procedures;[3] they were purged with dry nitrogen for 20–30 min prior to use to ensure oxygen removal.

Spectra and Analyses. Raman spectra were recorded on a Cary Model 82 laser Raman spectrometer equipped with a rotating-sample cell similar to that described elsewhere.[4] Unless otherwise noted, a slit width of 3 cm^{-1} and a scan rate equal to the ratio of the slit width to time constant were employed. Excitation was provided by Coherent Radiation Laboratory Model 52 argon and krypton ion lasers. Reported frequencies are precise to ± 1 cm^{-1}. Infrared spectra were recorded on a Perkin-Elmer Model 225 spectrophotometer employing either KBr disks or Nujol mulls supported on polyethylene plates. Frequencies are precise to ± 1 cm^{-1}. Optical spectra were obtained on sealed samples using a Cary Model 14 spectrophotometer. Raman intensities were determined by adding a known amount of internal standard (KNO_3) to a predetermined quantity of the desired complex. The resulting mixture was homogenized in a Spex Wig-L-Bug for 3–5 min. A polar planimeter was used to determine the intensity of each band of interest by integrating the area under each envelope and comparing it to the area of the 1049-cm^{-1} ν (A_1') band of the internal standard. All intensities were corrected for phototube response.

Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Tetrabromo- and tetrachlorotetrakis(tri-*n*-butylphosphine)dimolybdenum(II), $[(n\text{-}C_4H_9)_3P]_4Mo_2Br_4$ and $[(n\text{-}C_4H_9)_3P]_4Mo_2Cl_4$, were prepared as described previously.[5,6]

Bis-μ-(benzoato)-1,2-dichloro-1,2-bis(tri-*n*-butylphosphine)dimolybdenum(II), $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Cl_2$. $[(n\text{-}C_4H_9)_3P]_4Mo_2Cl_4$ (0.75 g, 0.66 mmol) was placed in a 100-ml flask equipped with a Teflon-coated stirrer bar and a condenser capped with a rubber septum. Benzoic acid (0.16 g, 1.3 mmol) was added and the condenser was attached. The system was flushed thoroughly with nitrogen before injecting benzene (10 ml) with a syringe. The resulting mixture was refluxed for 3 h and then concentrated by distillation to a volume of ~2 ml. Chilled (−15 °C) methanol (10 ml) was added to the cooled reaction mixture. The resulting orange precipitate was collected by suction filtration under nitrogen, rinsed with two 10-ml portions of ice-cold methanol followed by two 10-ml portions of ether, and dried in vacuo. The isolated yield was 58%. This compound is soluble in chloroform, acetone, and benzene.

Anal. Calcd for $C_{38}H_{64}Cl_2Mo_2O_4P_2$: C, 50.18; H, 7.09; Cl, 7.80; P, 6.81. Found: C, 50.09; H, 7.14; Cl, 7.90; P, 6.80.

Bis-μ-(benzoato)-1,2-dibromo-1,2-bis(tri-*n*-butylphosphine)dimolybdenum(II), $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$. This compound was obtained as orange-red crystals in 72% yield from the reaction of $[(n\text{-}C_4H_9)_3P]_4Mo_2Br_4$ (0.50 g, 0.38 mmol) and benzoic acid (0.093 g, 0.76 mmol) using a procedure analogous to that described for the preparation of $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Cl_2$. The solubility properties of the bromo and chloro complex are similar.

Anal. Calcd for $C_{38}H_{64}Br_2Mo_2O_4P_2$: C, 45.71; H, 6.46; Br, 16.01; P, 6.20. Found: C, 44.76; H, 6.18; Br, 15.68; P, 6.15.

1,2-Dibromo-1,2-bis(tri-*n*-butylphosphine)bis-μ-(2,4,6-trimethylbenzoato)-dimolybdenum(II), $[(n\text{-}C_4H_9)_3P]_2[2,4,6\text{-}(CH_3)_3C_6H_2CO_2]_2Mo_2Br_2$. Into a one-necked, 50-ml flask was placed 0.95 g (0.72 mmol) of $[(n\text{-}C_4H_9)_3P]_4Mo_2Br_4$, 0.24 g (1.46 mmol) of 2,4,6-trimethylbenzoic acid, and a Teflon-coated stirrer bar. The flask was then equipped with a condenser capped with a rubber septum, and the system was flushed with nitrogen. Benzene (15 ml) was added by means of a syringe, and the mixture stirred under reflux for 2 h. The solution was concentrated to approximately 5 ml and chilled (−15 °C) methanol (10 ml) was added by syringe. The resulting mixture was allowed to stand for 2 h. The crystalline, orange product which formed was collected by suction filtration, rinsed with two 5-ml portions of petroleum ether, and dried in vacuo. An isolated yield of 75% was obtained. This compound is soluble in chloroform and benzene.

Anal. Calcd for $C_{44}H_{76}Br_2Mo_2O_4P_2$: C, 48.81; H, 7.08; Br, 14.76; P, 5.72. Found: C, 48.61; H, 7.16; Br, 14.89; P, 5.90.

Tetrakis-μ-(benzoato)-dimolybdenum(II)–Bis(tri-*n*-butylphosphine), $(C_6H_5CO_2)_4Mo_2{\cdot}2P(n\text{-}C_4H_9)_3$. Tetrabromotetrakis(tri-*n*-butylphosphine)dimolybdenum(II) (0.50 g, 0.38 mmol) was placed in a 50-ml flask fitted with a condenser capped with a rubber septum. Benzoic acid (0.19 g, 1.6 mmol) was added to the flask, and the system was flushed with nitrogen before adding benzene (10 ml) by syringe. The resulting mixture was heated at reflux for 3 h and then allowed to stand at room temperature for 2 days. The red, crystalline precipitate that formed was collected by suction filtration under nitrogen and dried in a stream of dry nitrogen. The isolated yield was 79%. This material is air sensitive and cannot be recrystallized readily because of the labile nature of the coordinated phosphines.

Anal. Calcd for $C_{52}H_{74}Mo_2O_8P_2$: C, 57.78; H, 6.90; P, 5.73. Found: C, 56.75; H, 6.23; P, 5.59.

Bis-μ-(benzoato)-1,2-dibromo- and -1,2-dichloro-1,2-bis(trimethylphosphine)dimolybdenum(II), $[(CH_3)_3P]_2(C_6H_5CO_2)_2Mo_2X_2$. These compounds could not be prepared from $[(CH_3)_3P]_4Mo_2X_4$ utilizing procedures similar to those outlined for the preparation of the tri-*n*-butylphosphine analogues. They can, however, be prepared by the following typical procedure.

Bis-μ-(benzoato)-1,2-dibromo-1,2-bis(tri-*n*-butylphosphine)dimolybdenum(II), $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$ (0.70 g, 0.70 mmol), was placed in a 25-ml flask equipped with a condenser and a Teflon-coated stirrer bar. The condenser was capped with a serum stopper and the system flushed with nitrogen before injecting 5 ml of benzene. Trimethylphosphine (0.50 ml) was injected by syringe and an orange precipitate appeared immediately. The reaction mixture was gently refluxed for 15 min and then concentrated to half the original volume under nitrogen at room temperature; chilled (−20 °C) methanol (10 ml) was added and the orange precipitate collected by suction filtration, rinsed with 10 ml of chilled methanol, and dried in vacuo. The yield of $[(CH_3)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$ was virtually quantitative.

Anal. Calcd for $C_{20}H_{28}Cl_2Mo_2O_4P_2$: C, 36.55; H, 4.30; Cl, 10.79. Found: C, 36.79; H, 4.35; Cl, 10.90.

Tetrakis-μ-(benzoato)-dimolybdenum(II), $(C_6H_5CO_2)_4Mo_2$. Into a one-necked, 50-ml flask was placed tetrabromotetrakis(tri-*n*-butylphosphine)dimolybdenum(II) (1.00 g, 0.760 mmol), benzoic acid (0.38 g, 3.11 mmol), and a Teflon-coated magnetic stirrer bar. The flask was fitted with a condenser capped with a rubber septum and the system was flushed with nitrogen. Benzene (10 ml) was added via syringe and the mixture was refluxed for 3 h. A distillation head was attached and the solution was concentrated by distilling 8–10 ml of benzene under nitrogen. Chilled (−15 °C) methanol (10 ml) was added and the resulting mixture was stirred at −15 °C for 1 h. The yellow solid that formed was collected by suction filtration and washed with methanol (10 ml) followed by diethyl ether (10 ml). The isolated yield of $Mo_2(O_2CC_6H_5)_4$ was 59%. The spectral properties of this material were those observed for the equivalent material prepared by an alternative procedure.[7]

Anal. Calcd for $C_{28}H_{20}Mo_2O_8$: C, 49.72; H, 2.98. Found: C, 48.74; H, 2.92.

Tetrakis-μ-(acetato)-dimolybdenum(II), $(CH_3CO_2)_4Mo_2$. Tetrachlorotetrakis(tri-*n*-butylphosphine)dimolybdenum(II) (1.25 g, 1.09 mmol) was placed in a 50-ml flask containing a Teflon-coated stirrer bar. A condenser capped with a rubber septum was then attached. The system was flushed with nitrogen before injecting a solution of 0.50 ml (9.1 mmol) of acetic acid in 5 ml of benzene. After refluxing for 5 min, the mixture was cooled to room temperature and 10 ml of methanol was added. After standing at 0 °C for 2 h, the product was collected by suction filtration, washed with two 10-ml portions of absolute ethanol followed by two 10-ml portions of diethyl ether, and dried in vacuo. A yield of 62% was obtained.

Anal. Calcd for $C_8H_{12}Mo_2O_8$: C, 22.45; H, 2.83. Found: C, 22.59; H, 2.72.

Tetrakis-μ-(2,4,6-trimethylbenzoato)-dimolybdenum(II), $[2,4,6\text{-}(CH_3)_3C_6H_2CO_2]_4Mo_2$. Tetrabromotetrakis(tri-*n*-butylphosphine)dimolybdenum(II) (2.00 g, 1.51 mmol) and 2,4,6-trimethylbenzoic acid (1.00 g, 6.09 mmol) were placed in a 100-ml flask containing a Teflon-coated stirrer bar. A condenser capped with a rubber septum was attached, and the system was flushed with nitrogen before injecting 40 ml of benzene via syringe. The mixture was stirred under reflux for 3 h and then concentrated by distillation under nitrogen to a volume of ~6 ml. The resulting oil was treated with 10 ml of methanol. After standing at −15 °C for 1 h, the crystalline product was collected by suction filtration and washed with methanol until the washings appeared colorless. The isolated yield was 76%. This complex is soluble in acetone and diethyl ether.

Anal. Calcd for $C_{40}H_{44}Mo_2O_8$: C, 56.88; H, 5.25. Found: C, 56.84; H, 5.27.

Tetrakis-μ-(4-cyanobenzoato)-dimolybdenum(II), $(4\text{-}NCC_6H_4CO_2)_4Mo_2$. Into a one-necked, 50-ml flask was placed tetrabromotetrakis(tri-*n*-butylphosphine)dimolybdenum(II) (1.00 g, 0.760 mmol), 4-cyanobenzoic acid (0.450 g, 3.06 mmol), and a Teflon-coated magnetic stirrer bar. A condenser capped with a rubber septum was then attached and the system was flushed with nitrogen before injecting 20 ml of benzene by a syringe. After mixing under reflux for 2 h, the solution was concentrated by distillation to near dryness. The resulting oil was treated with diethyl ether (15 ml) and methanol (1 ml); the subsequent mixture was stirred for 15 min and then allowed to stand at −15 °C for 1 h. The red, crystalline solid which formed was collected by suction filtration, washed with two 10-ml portions of petroleum ether, and dried in vacuo. A yield of 71% was obtained. This material is soluble in acetone, acetonitrile, and methanol; it is insoluble in benzene and petroleum ether.

Anal. Calcd for $C_{32}H_{16}Mo_2N_4O_8$: C, 51.63; H, 2.17; N, 7.53. Found: C, 51.62; H, 2.24; N, 7,39.

Tetrakis-μ-(4-methoxybenzoato)-dimolybdenum(II), $(4\text{-}CH_3OC_6H_4CO_2)_4Mo_2$. $[(n\text{-}C_4H_9)_3P]_4Mo_2Br_4$ (1.00 g, 0.760 mmol) and 4-methoxybenzoic acid (0.480 g, 3.15 mmol) were placed in a 50-ml flask along with a Teflon-coated stirrer bar. A condenser capped with a rubber septum was attached and the system was flushed with nitrogen before injecting 20 ml of benzene by syringe. After mixing under reflux for 2 h, the solution was concentrated by distillation under nitrogen to a total volume of ~3 ml. Diethyl ether (15 ml) and methanol (1 ml) were then added to the resulting oil, and the mixture was allowed to stand for 15 min. The crystalline product that formed was collected by suction filtration, washed with two 10-ml portions of diethyl ether, and dried in vacuo. The isolated yield was 74%. This compound is soluble in acetone, chloroform, and methanol.

Anal. Calcd for $C_{32}H_{28}Mo_2O_{12}$: C, 48.26; H, 3.54. Found: C, 48.40; H, 3.46.

Tetrakis-μ-(butyrato)-dimolybdenum(II), $(CH_3CH_2CH_2CO_2)_4Mo_2$. Into a 100-ml flask equipped with a Teflon-coated stirrer bar was placed 1.00 g (0.76 mmol) of $[(n\text{-}C_4H_9)_3P]_4Mo_2Br_4$. A distillation head was attached and the system flushed thoroughly with nitrogen before injecting a deoxygenated solution of butyric acid (0.50 ml, 5.4 mmol) in benzene (10.0 ml) by syringe. The resulting mixture was gently refluxed under nitrogen with stirring for 2 h and then concentrated by distillation under nitrogen to a volume of ~3 ml. The pale yellow product which precipitated upon cooling was collected by filtration under nitrogen, washed with two 10-ml portions of

$$\underset{\mathbf{2}}{(R_3P)_2(C_6H_5CO_2)_2Mo_2X_2} \xleftarrow[C_6H_6,\ 80\ ^\circ C]{2C_6H_5CO_2H} \underset{\mathbf{1a}}{Mo_2X_4(PR_3)_4} \xleftarrow[CH_3OH,\ 60\ ^\circ C]{R_3P} \underset{\mathbf{1}}{Mo_2X_4L_4} \xrightarrow[C_6H_6,\ 80\ ^\circ C]{4C_6H_5CO_2H} \underset{\mathbf{3}}{(C_6H_5CO_2)_4Mo_2 \cdot 2L} \qquad (1)$$

petroleum ether, and finally dried in a stream of nitrogen. The isolated yield was 66%. The product, tetrakis-μ-(butyrato)-dimolybdenum(II), is extremely air sensitive and must be handled exclusively under nitrogen. A meaningful elemental analysis of this material could not be obtained because of its air sensitivity.

Tetrakis-μ-(4-methylbenzoato)- and tetrakis-μ-(3,5-dimethylbenzoato)-dimolybdenum(II), $(4\text{-}CH_3C_6H_4CO_2)_4Mo_2$ and $[3,5\text{-}(CH_3)_2C_6H_3CO_2]_4Mo_2$, were prepared from $[(n\text{-}C_4H_9)_3P]_4Mo_2Br_4$ (1.00 g, 0.760 mmol) and the respective benzoic acid, 4-methylbenzoic acid (0.414 g, 3.04 mmol) and 3,5-dimethylbenzoic acid (0.457 g, 3.04 mmol), by procedures similar to those described for the preparation of tetrakis-μ-(2,4,6-trimethylbenzoato)-dimolybdenum(II). Both compounds are air sensitive (the 3,5-dimethyl derivative exceedingly so) and are best handled exclusively under nitrogen.

Anal. Calcd for $C_{32}H_{20}Mo_2O_8$: C, 52.48; H, 3.85. Found: C, 52.41; H, 3.95. Calcd for $C_{36}H_{36}Mo_2O_8$: C, 54.83; H, 4.60. Found: C, 54.02; H, 4.65.

Results and Discussion

Synthesis. This study establishes that the complexes **1a**, L = PR_3 (R = C_2H_5, $n\text{-}C_4H_9$), undergo a series of ligand replacement reactions with benzoic acid in refluxing benzene. The extent of replacement depends on the ratio of the reactants. Partial replacement of halogen and phosphine results from the reaction of 2 mol of benzoic acid with 1 mol of **1a** and produces the mixed-halo-μ-benzoate complexes $(R_3P)_2(C_6H_5CO_2)_2Mo_2X_2$, **2**. A 4:1 ratio of benzoic acid to **1a**, L = $(n\text{-}C_4H_9)_3P$, results in complete halogen replacement and yields the bis(tri-*n*-butylphosphine) adduct of tetrakis-μ-(benzoato)-dimolybdenum(II), **3**. (See eq 1.) Both **2** and **3**, L = $(n\text{-}C_4H_9)_3P$, are soluble in a broad spectrum of organic solvents. However, dissolution of **3** in methanol, tetrahydrofuran, ether, or benzene is accompanied by its rapid conversion to tetrakis-μ-(benzoato)-dimolybdenum(II). Even extended treatment with pentane is sufficient to effect this transformation.

Surprisingly, the course of the ligand replacement sequence **1** → **1a** is strongly influenced by the nature of the phosphine ligand. Thus, for example, although the reaction of **1**, L = C_5H_5N, with $(n\text{-}C_4H_9)_3P$ in refluxing methanol is relatively facile, the analogous reaction of **1**, L = C_5H_5N, with $(C_2H_5)_3P$ under the same conditions is noticeably slower and **1**, L = C_5H_5N, is recovered unchanged after prolonged treatment with $(CH_3)_3P$ in refluxing methanol. In this instance, however, the desired complex **2**, L = $(CH_3)_3P$, can be prepared by taking advantage of the difference between the solubilities of **2**, L = $(n\text{-}C_4H_9)_3P$, and **2**, L = $(CH_3)_3P$, i.e.

$$[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2X_2 + 2(CH_3)_3P$$

$$\xrightarrow{C_6H_6} [(CH_3)_3P]_2(C_6H_5CO_2)Mo_2X_2\downarrow + 2(n\text{-}C_4H_9)_3P$$

Although tetrakis-μ-(carboxylato)-dimolybdenum(II) complexes, $(RCO_2)_4Mo_2$, have, in at least one instance,[8] been prepared from $(CH_3CO_2)_4Mo_2$ by carboxylate-exchange reactions, the principal synthetic route to these compounds has involved the direct interaction of carboxylic acids with molybdenum hexacarbonyl.[7,9] We have found that these same compounds can be prepared in comparable or better yields by the brief reaction of **1** with alkyl- and arylcarboxylic acids in warm benzene. Because the requisite starting complex **1** is also made indirectly from tetrakis-μ-(acetato)-dimolybdenum(II), there would seem to be little reason to employ such a synthetic sequence. However, the existing procedures, both direct and indirect, for the preparation of these compounds require prolonged reaction times and/or elevated temperatures. Moreover, these procedures are frequently efficient only when the corresponding acid is relatively abundant and can be used in large excess or when the product complex is relatively insoluble, thereby permitting its convenient isolation from the reaction mixture. Thus, for example, alkylcarboxylates such as tetrakis-μ-(butyrato)-dimolybdenum(II), whose solubility in a variety of organic solvents makes it a desirable complex for homogeneous studies of these compounds, cannot be efficiently prepared by existing procedures. In contrast, $(CH_3CH_2CH_2CO_2)_4Mo_2$ is readily obtained in an isolated yield of 66% by the direct reaction of **1** with a slight excess of butyric acid in refluxing benzene.

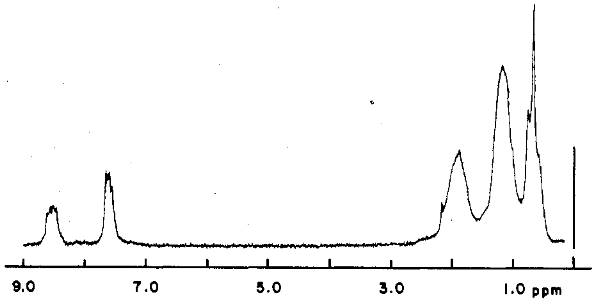


Figure 1. ^1H NMR spectrum (60 MHz, $CDCl_3$) of $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$.

^1H NMR Spectra. Figure 1 shows the ^1H NMR spectrum of a representative dihalo–bis-μ-benzoate complex, $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$. It is apparent that a total of four aryl and twelve methylene hydrogen atoms appear substantially deshielded relative to the position of the remaining aryl and methylene resonances. We have argued that such effects in dinuclear molybdenum(II) and rhenium(III) complexes are a direct consequence of the diamagnetic anisotropy that results when the circulating electrons within the metal-to-metal bond are subjected to an external field.[6] In view of these considerations and in light of the differing proximity of the various nonequivalent hydrogen atoms in **2** relative to the electrical center of gravity of the Mo–Mo bond,[10] it follows that these deshielded resonances correspond respectively to the ortho aryl protons (δ ~8.6) and the methylene protons (δ ~1.9) immediately adjacent to phosphorus. A meaningful ^1H NMR spectrum of **3** could not be obtained because of its instability in solution. Finally, related studies[10] reveal that the close proximity of the vicinal halogen to the coordinated phosphine in complexes such as **2** (and quite probably in related complexes such as **1a**) prevent the free rotation of the phosphine about the phosphorus–molybdenum bond. The significant broadening of the shifted α-methylene signal observed in both **1a** and **2** (cf. Figure 1) is a likely consequence of this fact.

Electronic Spectra. Each of the various classes of dimolybdenum(II) complexes exhibits a characteristic electronic absorption. Thus the tetra- and octahalo complexes $Mo_2X_4L_4$ and $Mo_2X_8^{4-}$ display maxima between ~500 and 700 nm (ε ~200–3000) that are responsible for the intense color associated with these compounds.[2] The probable similarity between the origin of this band and one of similar intensity and position observed for dinuclear rhenium(III) complexes was noted early in our studies.[6] Subsequently, Cowman and Gray, on the basis of an analogy to their studies with $Re_2Cl_6[P(C_2H_5)_3]_2$ but without direct experimental evidence, suggested this band corresponded to the $\delta \rightarrow \delta^*$ transition,[11] an assignment recently sustained by the single-crystal studies of Cotton et al.[12]

Table I summarizes the visible and near-uv data for a series of bis- and tetrakis-μ-(benzoato)-dimolybdenum(II) complexes.

Table I. Absorption Bands (300–700 nm) for Some Dinuclear Molybdenum(II) Carboxylates

Species	Medium	Absorption max,[a] nm
$(C_6H_5CO_2)_4Mo_2$	Ethanol	424 (18 440)[b]
$(C_6H_5CO_2)_4Mo_2$	Benzonitrile	423 (16 900)
$(C_6H_5CO_2)_4Mo_2$	Acetone	423 (21 700)
$(C_6H_5CO_2)_4Mo_2$	Dimethyl sulfide	426 (25 700)
$(C_6H_5CO_2)_4Mo_2$	THF	427 (22 400)
$(C_6H_5CO_2)_4Mo_2$	DMF[c]	436 (13 400)
$(C_6H_5CO_2)_4Mo_2$	Pyridine[c]	446 (13 700)
$(C_6H_5CO_2)_4Mo_2$	Tri-*n*-butylphosphine[c]	450 (>5000)
$(4\text{-}CH_3C_6H_4CO_2)_4Mo_2$	Acetone[c]	422 (>15 000)
$[3,5\text{-}(CH_3)_2C_6H_3CO_2]_4Mo_2$	Acetone	423 (16 250)
$[2,4,6\text{-}(CH_3)_3C_6H_2CO_2]_4Mo_2$	Acetone	366 (11 600)
$(4\text{-}CH_3OC_6H_4CO_2)_4Mo_2$	Acetone	417 (18 330)
$(4\text{-}NCC_6H_4CO_2)_4Mo_2$	Acetone	478 (25 700)
$(4\text{-}NCC_6H_4CO_2)_4Mo_2$	DMSO	506 (28 300)
$[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Cl_2$	Benzene	524 (1560)[d] 412 (9310)[e]
$[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$	Benzene	526 (1565)[d] 398 (9130)[e]
$[(n\text{-}C_4H_9)_3P]_2[2,4,6\text{-}(CH_3)_3C_6H_2CO_2]_2Mo_2Br_2$	Benzene	518 (1620)[d] 352 (8150)[e]

[a] Molar extinction coefficient, ε, in parentheses. [b] Dubicki and Martin[13] reported an extinction coefficient of 9000 for this band. [c] Repeated scans revealed a decrease in the intensity of this band with time, indicating sample instability in this solvent. [d] Assigned as δ → δ* transition. [e] The shape of this band envelope suggests incipient resolution of an undetermined origin.

Two specific points concerning these data are noteworthy. First, the dihalo complexes $[(n\text{-}C_4H_9)_3P]_2(RCO_2)_2Mo_2X_2$ display two characteristic, relatively intense electronic bands between 400 and 600 nm. On the basis of the close similarity in energy and intensity of the *lower* frequency band to the $\delta \rightarrow \delta^*$ band in the tetrahalo series described above, we assign this band a similar origin in these complexes.

Second, the electronic spectra of the tetrakis-μ-(carboxylato) complexes offer a distinct contrast to the uv–visible spectra observed for the di-, tetra-, and octahalo complexes. Specifically, the lowest energy visible absorption band for several tetrakis-μ-(alkylcarboxylates) occurs at ~430 nm with a molar extinction coefficient of ~60 cm^{-1} M^{-1}. In addition, there appear two higher energy maxima at ~300 nm (ϵ ~8000) and 230 nm (ϵ ~4000). These spectral parameters are quite similar to those previously reported[12a,13] and are apparently representative of the tetrakis-μ-(alkylcarboxylato)-dimolybdenum(II) systems in general. The origin of the weak, lowest energy band has been studied by Cotton and Martin,[12a] who, on the basis of polarized single-crystal studies of the compound $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2\cdot 2H_2O$, have concluded that this absorption band *cannot* be assigned to the $\delta \rightarrow \delta^*$ transition.

The visible spectra of tetrakis-μ-(*aryl*carboxylates) of dimolybdenum(II) are a marked contrast to those observed for tetrakis-μ-(*alkyl*carboxylate) complexes. In particular, the lowest energy transition(s) in these complexes is (are) a broad, intense band centered between 350 and 480 nm (ϵ >16 000) (cf. Figure 2). It is clear from the data in Table I that this maximum is generally characteristic of tetrakis-μ-(arylcarboxylate) complexes of dimolybdenum(II). Moreover, these same data reveal that the donor nature of the solvent has a pronounced influence on the position of this band in $(C_6H_5CO_2)_4Mo_2$. We believe that this effect is primarily the result of axial donor adduct formation. This suggestion is supported by the considerable variation in band intensity that accompanies changes in solvent donor character, a clear indication of donor–acceptor interaction, as well as by the isolation of what we believe to be the bis(tri-*n*-butylphosphine) axial adduct of $(C_6H_5CO_2)_4Mo_2$.[14] Except for a very qualitative relationship between solvent donor character and the magnitude of the spectral shift in $(C_6H_5CO_2)_4Mo_2$, a spectrochemical relationship such as that observed between ligand π-acceptor character and the position of the $\delta \rightarrow \delta^*$ band in $Mo_2X_4L_4$ and similar complexes bearing radially disposed ligands[5] is not evident in the axially coordinated adducts of $(C_6H_5CO_2)_4Mo_2$.

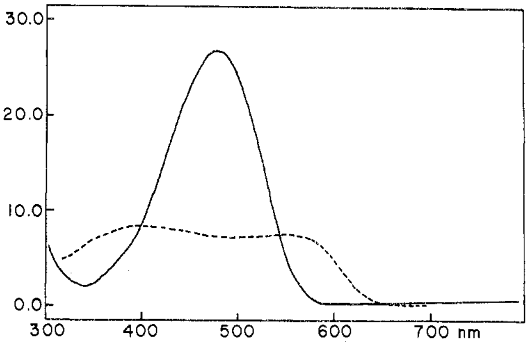


Figure 2. Electronic spectra of $(4\text{-}NCC_6H_4CO_2)_4Mo_2$: absorption spectrum ($3.1 \times 10^{-5}$ M) recorded in acetone, solid line; reflectance spectrum obtained as a KBr pellet, dashed line.

Although a definitive assignment of the origin of the broad band which characterizes the optical spectra of the tetrakis-μ-(arylcarboxylates) is unavailable, certain observations concerning its behavior are noteworthy. Specifically, the influence which aryl substituents have on the position and intensity of this band bears brief mention. It is well-known that the interaction between para substituents in a benzene ring occurs principally through the π-donating and π-accepting functionalities when substituted in the para position of a benzene ring. In light of the considerable difference (~60 nm) between the position of the maxima observed for $(4\text{-}CH_3OC_6H_4CO_2)_4Mo_2$ and $(4\text{-}NCC_6H_4CO_2)_4Mo_2$, it follows that whatever the origin(s) of this transition, there is appreciable π interaction between the benzene ring and the principal chromophore responsible for this absorption. Since neither *p*-cyano- nor *p*-methoxybenzoic acid has any electronic bands in this region, it is reasonable to conclude that the chromophore responsible for this absorption involves, in some way, the molybdenum centers. It further follows that there is substantial (p–d)π interaction between the benzene ring and these metal centers, presumably through the agency of the bridging carboxylate moieties. This conclusion is supported by the fact that the dimolybdenum–carboxylate–aryl groups in $[(n\text{-}C_4H_9)_3P](C_6H_5CO_2)_2Mo_2Br_2$ and presumably also in $(C_6H_5CO_2)_4Mo_2$ and related complexes reside in an essentially planar geometry.[10] In view of the currently accepted description of orbital construction in the Mo_2^{4+} ion,[2,15] such an arrangement would allow maximum π-orbital overlap between these centers. This view also provides a reasonable explanation for an apparent anomaly, viz., the considerable difference observed between the position of the maximum for tetrakis-μ-(benzoato)-dimolybdenum(II) (423 nm) and that exhibited by tetrakis-μ-(2,4,6-trimethylbenzoato)-dimolybdenum(II) (366 nm). The possibility that this shift is a result of the multiple inductive effect brought about by the substitution of three methyl groups on the benzene ring cannot be completely dismissed but must be considered unlikely in view of the fact that λ_{max} for $[C_6H_5CO_2]_4Mo_2$, $[4\text{-}CH_3C_6H_4CO_2]_4Mo_2$, and $[3,5\text{-}(CH_3)_2C_6H_3CO_2]_4Mo_2$ are essentially the same. A more attractive explanation is that the shift to higher energy is a consequence of the reduction in π interaction between the bridging carboxylate groups and the benzene ring brought about by the steric-induced departure of these elements from the planar geometry enjoyed in $(C_6H_5CO_2)_4Mo_2$.

Table II. Selected Solid-State Raman Frequencies (cm^{-1}) of Bis- and Tetrakis-μ-(benzoato)-dimolybdenum(II) Complexes[a,b]

$[(n\text{-}C_4H_9)_3P]_2$-$(C_6H_5CO_2)_2Mo_2Cl_2$[c]	$[(n\text{-}C_4H_9)_3P]_2$-$(C_6H_5CO_2)_2$-Mo_2Br_2[d]	$[(n\text{-}C_4H_9)_3P]_2$-$[2,4,6\text{-}(CH_3)_3$-$C_6H_2CO_2]_2Mo_2Br_2$[c]	$[2,4,6\text{-}(CH_3)_3$-$C_6H_2CO_2]_4Mo_2$[c]	$(4\text{-}NCC_6H_4$-$CO_2)_4Mo_2$[c]	$(4\text{-}CH_3OC_6$-$H_4CO_2)_4Mo_2$[c]
1604 s	1603 s	1610 w	1614 m	1607 m	1606 w–m
1501 s	1498 s	1525 vw, br	1587 vw	1504 w–m	1550 w
1458 vw	1444 m	1481 m	1481 m	1410 vs	1519 m–s
1420 sh	1404 vs	1437 m	1448 sh	1181 w	1475 vw
1408 vs	1386 sh	1388 s	1436 s	1016 vw	1456 vw
1390 sh	1179 w	1293 vw	1385 vs	768 vw	1441 w
1180 w	1004 w	1141 w, br ($3\nu_1$)	1293 w	603 vw	1418 vs
1146 vw	760 vw, br	764 m ($2\nu_1$)	1188 vw	437 vw	1395 s
1004 w	695 w	627 w	1114 vw	*397 w–m*	1380 sh, vw
773 vw, br	495 m	572 vw	1024 vw	158 vw	1184 w
694 w	*383 w–m*	532 vw	631 w		1173 w
500 m		521 vw	576 vw		1148 vw
392 w–m		482 vw	520 vw		1014 vw
		454 w	462 w		867 vw
		383 (ν_1)	450 w		790 vw
		302 vw	*404 w–m*		647 vw
		248 vw	304 vw		633 vw
		224 w	212 vw		516 vw
		212 vw	150 w		441 w
		142 vw			431 w
					402 w–m
					152 w

[a] Qualitative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad. [b] The frequencies assigned to ν(Mo–Mo) are shown in italics. [c] Obtained using 4880-Å exciting radiation. [d] Recorded using 4762-Å exciting radiation.

Table III. Selected Infrared Frequencies (cm^{-1}) of Some Bis-μ-(arylcarboxylato)-dihalodimolybdenum(II) Complexes[a]

$[(n\text{-}C_4H_9)_3P]_2$-$(C_6H_5CO_2)_2Mo_2Cl_2$	$[(n\text{-}C_4H_9)_3P]_2$-$(C_6H_5CO_2)_2Mo_2Br_2$	$[(n\text{-}C_4H_9)_3P]_2$-$[2,4,6\text{-}(CH_3)_3$-$C_6H_2CO_2]_2Mo_2Br_2$	$[2,4,6\text{-}(CH_3)_3$-$C_6H_2CO_2]_4Mo_2$	$(4\text{-}CH_3OC_6$-$H_4CO_2)_4Mo_2$	$(4\text{-}NCC_6H_4$-$CO_2)_4Mo_2$
1600 m	1600 w	1607 m	1688 w, br	1685 m	2242 sh
1487 s	1501 s	1569 vw	1608 m	1604 vs	2230 m
1478 s	1490 s	1520 vw	1569 w	1584 m	1702 w
1464 m	1466 m	1461 s	1484 s	1528 sh	1603 w
1455 m	1458 m	1432 s	1438 s	1511 m	1579 w
1436 m	1442 m	1383 vs	1431 s	1483 m	1506 s
1420 sh	1404 vs	1335 vw	1387 sh	1451 m	1400 vs
1403 vs	1341 vw	1300 vw	1379 s	1425 sh	1292 w
1343 vw	1215 w	1290 vw	1287 w	1399 vs	1251 vw
1215 w	1179 w	1278 vw	1177 m	1330 sh	1177 vw
1208 w	1158 w	1224 vw	1163 sh	1312 sh	1146 vw
1182 w	1141 vw	1203 w	1107 m	1302 m	1135 vw
1170 w	1096 m	1182 w–m	1085 w	1261 vs	1111 vw
1157 m	1071 m	1107 w–m	1031 w	1178 sh	967 vw
1140 w	1027 m	1094 w	976 w	1170 vs	911 vw
1095 m	972 w	1046 vw	847 m	1149 w	859 m
1070 m	937 vw	969 w	826 w	1128 vw	846 w
1059 w	914 m	910 w–m	791 w	1105 w	768 s
1028 m	847 m	851 m	725 w, br	1028 m	761 sh
1005 w	808 w	828 m	706 w	947 w–m	693 m
967 w	781 w	792 w	623 sh	924 w	643 vw
940 vw	722 vs	746 vw	610 m	850 sh	613 sh
907 w	684 s	717 w–m	568 w	844 m	587 m
844 m	491 m	622 sh	456 m	819 w	546 m
811 w	385 w	611 m		780 sh	439 vw
781 m		565 vm		772 s	386 vw
727 vs		455 m		730 w, br	
681 s		380 vw		697 w	
491 m		333 vw, br		634 m	
384 w				621 m	
306 s ν(Mo–Cl)				614 sh	
				549 w	
				515 w	
				506 w	
				441 w	
				393 w	

[a] Recorded in KBr matrix. Qualitative intensities as in Table II.

The direction of the observed shift is consistent with this conclusion.

Vibrational Spectra. Earlier studies have shown that the Raman spectra of **1** and related complexes exhibit a band at ~345 cm^{-1} attributable to the Mo–Mo stretching vibration.[5] For $(CH_3CO_2)_4Mo_2$, this band appears at considerably higher frequency (406 cm^{-1}). Table II summarizes the solid-state Raman spectra of a series of bis-μ-(arylcarboxylato)-dihalodimolybdenum(II) compounds. All spectra reveal a single band of medium to weak intensity within a frequency range

Table IV. Integrated Intensity Ratios Observed for ν(Mo–Mo), $\nu_s(CO_2)$, and $\nu_{as}(CO_2)$ in Solid $(4\text{-}NCC_6H_4CO_2)_4Mo_2$[a]

Excitation wavelength, Å	$I_{M-M}/I_{NO_3^-}$ [b]	$I_{CO_2(s)}/I_{NO_3^-}$ [c]	$I_{CO_2(as)}/I_{NO_3^-}$ [b]
4765	4.3	3.1	3.1
4880	5.1	4.0	3.6
4965	5.5	5.0	4.6
5145	7.6	8.1	6.2
5309	16	8.9	7.6
5682	12	6.2	4.0
6471	5.4	2.1	2.0

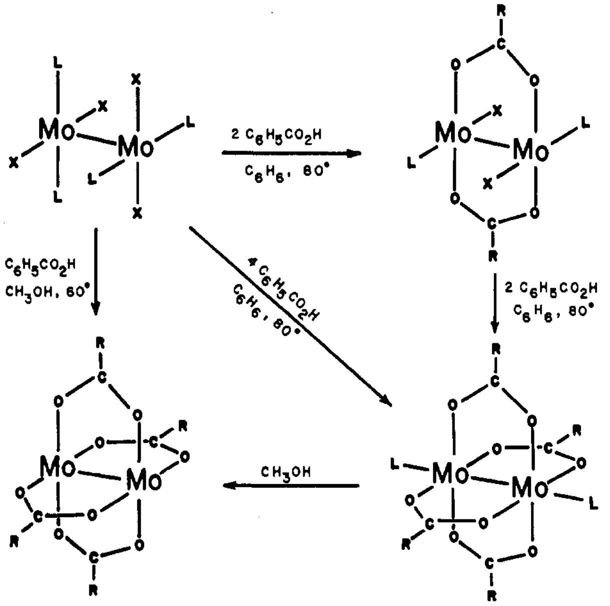
[a] Corrected for relative phototube response. Samples were prepared by homogenizing 0.30 mol % $(4\text{-}NCC_6H_4CO_2)_4Mo_2$ and 99.7 mol % potassium nitrate (as internal standard) and the resulting mixture was pressed into a pellet. [b] Multiplied by 10^{-2}. [c] Multiplied by 10^{-3}.

appropriate for ν(Mo–Mo). Severe fluorescence was encountered with these compounds, and the only spectra which could be determined were those recorded using exciting frequencies on the remote, high-energy side of the $\delta \rightarrow \delta^*$ maximum. Consequently, we were unable to obtain an excitation profile which might have permitted a more definitive assignment of the metal–metal stretching frequency in these complexes. A summary of selected infrared data for several bis-μ-(arylcarboxylato)-dimolybdenum(II) complexes is presented in Table III.

As discussed above, the electronic spectra of the tetrakis-μ-(carboxylato) complexes of dimolybdenum(II) are characterized by a single rather broad envelope, which, in the case of $(4\text{-}NCC_6H_4CO_2)_4Mo_2$, exhibits a maximum in acetone solution at 478 nm. Such a band is conveniently accessible to the plasma lines of the krypton and argon ion lasers and Table IV summarizes the variations in relative intensities observed for three modes: ν(Mo–Mo) at 391 cm^{-1}, $\nu_s(CO_2)$ at 1406 cm^{-1} and $\nu_{as}(CO_2)$ at 1501 cm^{-1}. Regrettably, the instability of $(4\text{-}NCC_6H_4CO_2)_4Mo_2$ in solution precluded accurate studies under these conditions. The data presented in Table IV were obtained on solid-state samples. They reveal that the intensities of both the metal–metal and carboxylate stretching vibrations are substantially enhanced over the range of exciting frequencies employed. The intensity enhancement in all three vibrations reaches a maximum between 514 and 568 nm. It follows that the Mo–Mo and carboxylate modes are in resonance with the electronic transition centered in this region. Although the electronic spectrum of $(4\text{-}NCC_6H_4CO_2)_4Mo_2$ in acetone solution (Figure 2) does not display a band in this region, as noted by others,[16] the maximum in an excitation profile correlates with the effective absorption frequency which, particularly in the solid state, is not necessarily the maximum observed for the solution uv–visible absorption data. The reflectance spectrum of $(4\text{-}NCC_6H_4CO_2)_4Mo_2$ in KBr supports this contention. It clearly shows (Figure 2) a low-energy band centered at ~565 nm.[17] The position of this band correlates well with the maximum in the excitation profile. The difference between the solid-state reflectance spectrum and the solution uv–visible spectrum is considerable but not unreasonable in view of the substantial influence which solvent donor character has on the solution spectra of $(C_6H_5CO_2)_4Mo_2$ and related complexes (Table I). The origin of the higher energy band in the reflectance spectrum in not obvious. It is not observed in the solution spectrum of reclaimed samples.[17]

These data are sufficient to establish that both the 1406-cm^{-1} symmetric carboxylate stretching vibration and the 391-cm^{-1} molybdenum–molybdenum stretching vibration are each in resonance with (possibly the same) electronic transition centered at ~565 nm. We conclude that the principal low-energy transition in $(4\text{-}NCC_6H_4CO_2)_4Mo_2$ must involve a significant and possibly simultaneous[19] change in the occupancy of the metal–metal and carboxylate orbitals. If so, it follows that a common molecular orbital is involved.

Scheme I. Chemical and Structural Relationships That Exist between Some Dinuclear Molybdenum(II) Complexes[a]



[a] The structure of $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$ is described in detail in the following paper.[10]

Summary

This paper reports the preparation and characterization of a series of bis- and tetrakis-μ-(carboxylates) of dinuclear molybdenum(II). The former constitute a new class of dinuclear complexes. The chemical and structural relationships that exist between these compounds are summarized in Scheme I. From the spectroscopic point of view, several observations of a qualitative nature have emerged. These include the considerable influence of solvent donor character on the position and intensity of the intense band that characterizes the optical spectrum of tetrakis-μ-(carboxylates) as well as a partial indication of the basic nature of this transition. Although qualitative, these observations are relevant to the currently unresolved question of the detailed electronic structures[2,15] of these and related complexes.

Registry No. $(C_6H_5CO_2)_4Mo_2$, 24378-22-1; $(4\text{-}CH_3C_6H_4CO_2)_4Mo_2$, 33637-86-4; $[3,5\text{-}(CH_3)_2C_6H_3CO_2]_4Mo_2$, 59671-89-5; $[2,4,6\text{-}(CH_3)_3C_6H_2CO_2]_4Mo_2$, 59671-90-8; $(4\text{-}CH_3OC_6H_4CO_2)_4Mo_2$, 33637-87-5; $(4\text{-}NCC_6H_4CO_2)_4Mo_2$, 59671-91-9; $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Cl_2$, 59671-92-0; $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$, 59493-09-3; $[(n\text{-}C_4H_9)_3P]_2[2,4,6\text{-}(CH_3)_3C_6H_2CO_2]_2Mo_2Br_2$, 59671-93-1; $[(CH_3)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$, 59671-94-2; $(CH_3CO_2)_4Mo_2$, 14221-06-8; $(CH_3CH_2CH_2CO_2)_4Mo_2$, 41772-56-9; $[(n\text{-}C_4H_9)_3P]_4Mo_2Cl_4$, 38832-72-3; $[(n\text{-}C_4H_9)_3P]_4Mo_2Br_4$, 51731-44-3; $(C_6H_5CO_2)_4Mo_2\text{-}2P(n\text{-}C_4H_9)_3$, 59671-95-3.

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Crystal and Molecular Structure of Bis-μ-(benzoato)-1,2-dibromo-1,2-bis(tri-*n*-butylphosphine)dimolybdenum(II), $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$

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The crystal structure of the title compound has been determined by a single-crystal three-dimensional x-ray diffraction study. The structure consists of discrete centrosymmetric $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$ units, each with a short Mo–Mo bond length [2.091 (3) Å] indicative of a strong bond. Each Mo atom is also bonded to a bromine atom, to a phosphorus atom, and to two bridging carboxylate oxygen atoms. The disposition of the former ligands is similar to that reported for $Re_2Cl_6[P(C_2H_5)_3]_2$. Short contacts between the α-methylene atoms of the tri-*n*-butylphosphine ligand and the bromide ligand give rise to relatively large Mo′–Mo–Br and Mo′–Mo–P angles [115.9 (1) and 101.9 (1)°, respectively], and the molybdenum coordination geometry may be described formally as distorted trigonal bipyramidal. It is concluded that these interactions must result in a reduction in the freedom of rotation about the P–Mo bond. This conclusion is sustained by an examination of the ^1H NMR spectrum of the trimethylphosphine analogue, $[(CH_3)_3P]_2(C_6H_5CO_2)_2Mo_2X_2$, which exhibits two nonequivalent methyl resonances at ambient temperatures. Short contacts are also observed between the α carbon atoms and the carboxylate oxygen atoms. Several of the α- and β-methylene protons, as well as the ortho phenyl protons, lie in close proximity to the center of the Mo–Mo bond. They are, therefore, in geometrically favorable positions to be influenced strongly by the anisotropic induced magnetic field of the Mo–Mo bond. Crystallographic data are as follows: space group $P2_1/c$; unit cell $a = 12.17$ (1), $b = 11.21$ (1), $c = 17.95$ (1) Å; $\beta = 114.7$ (1)°; $V = 2225$ Å^3; d_{calcd} for $Z = 2$ is 1.49 and d_{obsd} is 1.49 (2) g/cm^3. Diffractometer data (1582 independent reflections with $F^2 \geq 3\sigma$) were used to refine the structure to final values of $R_F = 0.073$ and $R_{wF} = 0.090$.

Introduction

For several years, we have maintained a continuing interest in compounds with metal-to-metal bonds, with particular emphasis on the chemistry of dinuclear molybdenum(II) complexes.[1-6] Physical–chemical studies of these compounds, aimed at clarifying the nature of ligand substitution processes and geometric isomerism[3] as well as the origin of certain spectroscopic features,[3] are currently in progress. Before embarking upon this undertaking, however, we deemed it desirable to firmly establish the structures of several key complexes.

Cotton and co-workers[7] have reported the x-ray structures of a number of dimolybdenum(II) complexes including $Mo_2Cl_8^{4-}$, $Mo_2(CH_3)_8^{4-}$, and several μ-carboxylato and μ-sulfanato species. Our work has centered around the di- and tetrahalo complexes of Mo_2^{4+}, and for these, definitive structural data are unavailable. The structure of a bromo complex would be particularly interesting since the parent species, $Mo_2Br_8^{4-}$, is unknown. These facts, together with our inability to otherwise assign the structure of $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$ unambiguously, prompted the present investigation.

Experimental Section

The preparation of the complex is described in the previous paper.[6] Crystals suitable for x-ray analysis were obtained by slow evaporation from acetone. A crystal approximately 0.18 × 0.20 × 0.35 mm was mounted in a sealed glass capillary parallel to the crystal axis *b*. Weissenberg photographs indicated space group $P2_1/c$ with systematic absences of $h0l$ when $l = 2n + 1$ and of $0k0$ when $k = 2n + 1$. Unit cell parameters $a = 12.17$ (1) Å, $b = 11.21$ (1) Å, $c = 17.95$ (1) Å, and $\beta = 114.7$ (1)° were obtained from a least-squares fit of 12 reflections using graphite-monochromated Mo Kα radiation (λ 0.710 69 Å) and an Enraf-Nonius CAD-3 automated diffractometer. The unit cell volume is 2225 Å^3. A density of 1.49 g/cm^3 was calculated for $Z = 2$, and this agreed with that of 1.49 (2) g/cm^3 measured by flotation in aqueous ZnI_2 solution.

Data were collected at room temperature (23 ± 2 °C) using graphite-monochromated Mo Kα radiation and techniques described previously.[4] The intensity of a standard reflection, measured at 50 reflection intervals, showed a maximum deviation of ±6%, and an average deviation of 2.6%. This rather large deviation was traced primarily to temperature fluctuations in the room beyond the control of the experimenters; it caused slight misalignment of the crystal. The crystal was realigned periodically, and a total of 3180 independent reflections were collected in the range $2 < \theta < 25°$. The data were placed on a common scale by correcting for the above deviation and for Lorentz and polarization effects. Absorption corrections were not applied. For Mo Kα radiation, $\mu = 25.6$ cm^{-1} and calculated transmission coefficients ranged from 0.61 to 0.72. Standard deviations were assigned to F^2 values according to

$$\sigma(F^2) = \frac{1}{Lp}\left[N_t + (0.02N_n)^2\right]^{1/2}$$

where N_t is the total count, N_n is the net count, and 0.02 is an estimate of instrumental instability. Of the measured reflections, 1582 with $F^2 \geq 3\sigma$ were used for the structure solution and refinement.