Identification of an Entire Family of Dimolybdenum(II) Mixed-carboxylato Complexes $(C_6H_5CO_2)_nMo_2(CH_3OCH_2CO_2)_{4-n}$ (n = 0–4) in a Single Reaction Mixture

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(Received March 27, 1987)

Experimental

All reactions were carried out in an atmosphere of nitrogen. Methoxyacetic acid $CH_3OCH_2CO_2H$ was purchased from Aldrich and used without further purification. $(CH_3CO_2)_4Mo_2$ [1] and $(C_6H_5CO_2)_4Mo_2$ [2] were synthesized according to literature procedures.

Preparation

$(CH_3OCH_2CO_2)_4Mo_2$ (5)

To a suspension of $(CH_3CO_2)_4Mo_2$ (0.25 g, 0.58 mmol) in dry methanol (20 ml) was added $CH_3OCH_2CO_2H$ (0.9 g, 9.99 mmol). The resulting light-brown solution was refluxed for 5 h. On cooling the product precipitated as a yellow solid.

Solid mixture A comprising the five complexes 1–5 of formula $(C_6H_5CO_2)_nMo_2(CH_3OCH_2CO_2)_{4-n}$ (n = 0–4)

To a yellow suspension of $(C_6H_5CO_2)_4Mo_2$ (0.25 g, 0.37 mmol) in dry methanol (20 ml) was added $CH_3OCH_2CO_2H$ (0.9 g, 9.99 mmol). The mixture was refluxed for 4 h and at all times a yellow solid was present in the reaction flask. After cooling to room temperature the yellow product mixture A was filtered off.

Results and Discussion

The tetrakis-μ-(alkylcarboxylato)dimolybdenum(II) complex $(CH_3CO_2)_4Mo_2$ reacts with excess $CH_3OCH_2CO_2H$ to give the tetra-substituted product $(CH_3OCH_2CO_2)_4Mo_2$ (5). No intermediate mixed-carboxylato complexes were isolated. In contrast, under similar experimental conditions the arylcarboxylato complex $(C_6H_5CO_2)_4Mo_2$ reacted with

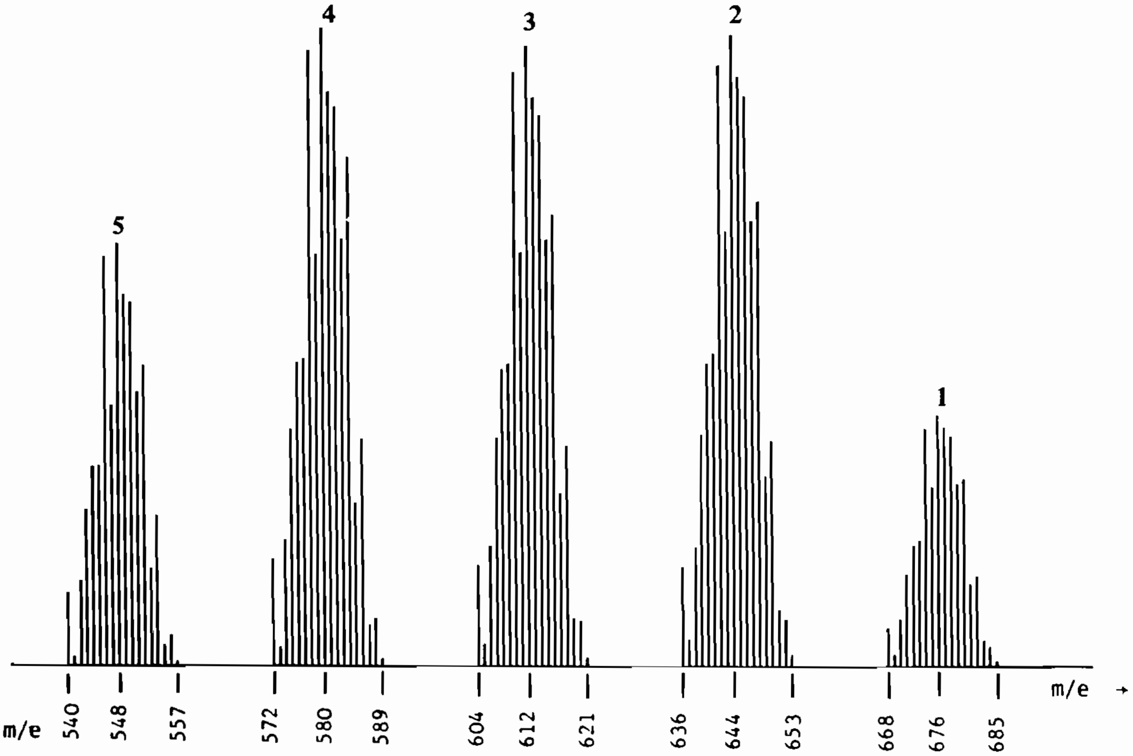

Fig. 1. Mass spectrum of mixture A showing the observed isotope ratios for the molecular ions of each of the five constituent complexes (1–5) present in the mixture.

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0020-1693/87/$3.50

TABLE I. Mass Spectral Data for Product Mixture A

Complex	Degree of substitution	Species	m/e[a]
1	un-substituted	$(C_6H_5CO_2)_4Mo_2^+$	676
2	mono-substituted	$(C_6H_5CO_2)_3Mo_2(CH_3OCH_2CO_2)^+$	644
3	di-substituted	$(C_6H_5CO_2)_2Mo_2(CH_3OCH_2CO_2)_2^+$	612
4	tri-substituted	$(C_6H_5CO_2)Mo_2(CH_3OCH_2CO_2)_3^+$	580
5	tetra-substituted	$(CH_3OCH_2CO_2)_4Mo_2^+$	548

[a] Ions shown are those with molybdenum atom weights totalling 192 amu.

excess $CH_3OCH_2CO_2H$ to give a five-product solid mixture A. The mass spectrum of A showed five distinct molecular ion peaks (Fig. 1) corresponding to the five products **1**–**5** of formula $(C_6H_5CO_2)_n$-$Mo_2(CH_3OCH_2CO_2)_{4-n}$ ($n = 0$–4), Table I. It should also be noted that $(C_6H_5CO_2)_2Mo_2(CH_3OCH_2CO_2)_2$ (**3**) can exist as *cis*- and *trans*-isomers. The large number of naturally occurring abundant isotopes for molybdenum and the presence of two molybdenum atoms in each molecule resulted in molecular ions each with 18 different peaks with distinctive ratios one to another. This pattern is a 'fingerprint' for complexes containing the Mo_2^{+4} core [3]. Complexes **1**–**5** are representative of all the various degrees of substitution of the original four benzoato ligands in $(C_6H_5CO_2)_4Mo_2$ with methoxyacetato ligands. The five molecular ions were the most abundant ions in the mass spectrum and there was no evidence corresponding to fragments containing a single molybdenum ion. This feature was consistent with that reported for the mass spectrum of $(CH_3CO_2)_4Mo_2$ [3]. In the chemistry of bimetallic carboxylato complexes this is the first time that complexes representing all the possible degrees of substitution have been positively identified in a product mixture.

It is noteworthy that on increasing the molar ratio of $CH_3OCH_2CO_2H$:$(C_6H_5CO_2)_4Mo_2$ and/or prolonging the reflux time the composition of the solid mixture A did not vary. These observations are consistent with those reported by Cotton and Thompson for the reaction of $(CH_3CO_2)_4Rh_2$ with excess triphenylacetic acid [4]. These workers found that the sole product of this reaction was the di-substituted, mixed-carboxylato species $(CH_3CO_2)_2$-$Rh_2(Ph_3CCO_2)_2(CH_3CN)_2C_6H_5CH_3$.

As yet no definitive explanation (*i.e.* kinetic or thermodynamic control) can be offered as to why $(C_6H_5CO_2)_4Mo_2$, on reaction with methoxyacetic adic, yields a mixture of unsubstituted, mono-, di-, tri- and tetra-substituted products, whereas $(CH_3CO_2)_4Mo_2$ affords only the tetra-substituted product. It is interesting to note that when San Filippo and Sniadoch [5] treated $(PBu^n{}_3)_4Mo_2X_4$ ($X = Cl$ or Br) with controlled amounts of benzoic acid one of three complexes, *viz.* $(C_6H_5CO_2)_4Mo_2$, $(C_6H_5CO_2)_4Mo_2(PBu^n{}_3)_2$ or $(C_6H_5CO_2)_2Mo_2(PBu^n{}_3)_2X_2$ could be isolated according to the reaction conditions. Under similar conditions alkyl carboxylic acids formed only the tetra-substituted product $(RCO_2)_4Mo_2$.

A sample of mixture A has been shown to be catalytically active towards the ring-opening polymerization of norbornene [6]. Pure $(CH_3OCH_2CO_2)_4Mo_2$ is also a catalyst for this polymerization reaction [6].

Supplementary Material

Additional material (preparative, analytical, IR and MS data) is available from the Editor-in-Chief, *Inorganica Chimica Acta*, Padua, Italy.

Acknowledgements

We thank the Microanalytical Laboratory, University College Cork, Cork, Ireland for microanalysis, and Professor J. J. Rooney, Queen's University, Belfast for supplying the mass spectrum. A postgraduate research grant to H. Ryan from the Tipperary S. R. County Council, Ireland is also acknowledged.

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