

## MASS SPECTRAL STUDIES ON MIXED LIGAND QUADRUPLY BONDED MOLYBDENUM COMPLEXES COMPARISON WITH THE HOMOLIGAND PARENT COMPOUNDS

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(Received November 18, 1992; revised June 28, 1993)

The EI mass spectrum of the mixed ligand quadruply bonded molybdenum complexes  $\text{Mo}_2(\text{O}_2\text{CCF}_3)_2(\text{S}_2\text{PF}_2)_2$  and  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{S}_2\text{PF}_2)_2$  show fragments which are observed in the mass spectrum of the parent homoligand compounds. The fragmentation of  $\text{Mo}_2(\text{O}_2\text{CCF}_3)_2(\text{S}_2\text{PF}_2)_2$  is similar to that of the parent compound  $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ .  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{S}_2\text{PF}_2)_2$  on the other hand show fragment that is not observed in the mass spectrum of the parent compound,  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ . The acetato bridged mixed ligand complex show fragments containing one molybdenum atom resulting from the cleavage of the metal-metal bond, a process not observed in the mass spectrum of the parent compound,  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ .

**Key words:** Mass spectrum, Molybdenum complex, Dithio-phosphinate acetate ligands.

### Introduction

Molybdenum exhibits a large number of oxidation states among which the +2 state is specially important since the metal ions in this oxidation state form complexes containing multiple metal-metal bond [1-5]. The small metal-metal bond distance in such compounds as  $\text{K}_4\text{Mo}_2\text{Cl}_8$  (2.139 Å) [6], compared to single-bond distances, supports the view of the multiple nature of the Mo-Mo bond formed by the overlap of appropriate metal d-orbitals. Characterization of compounds containing multiple Mo-Mo bonds is done mainly by X-ray crystallography, IR, Raman Spectroscopy, EPR and NMR methods [7,8]. For some molybdenum complexes, good elemental analysis results were not obtained although other methods conclusively characterized those compounds [9,10]. In such cases where a good crystal is not obtainable for crystal structure determination and the result of elemental analysis is not excellent, the mass spectral data may offer an insight into the composition and structural features of those compounds.

There has been very few reports [11,12] on the mass spectra of complexes containing  $\text{Mo}_2$  units. The molecular ion peak and well separated peaks for fragments help in characterizing these compounds from their mass spectra. The presence of a large number of isotopes of Mo atoms with a natural abundance lying between 9 and 24, results in a 15 line peak pattern for fragments containing  $\text{Mo}_2$  units. Although this complicates the spectrum, the isotopic combination can be used to characterize the fragments having  $\text{Mo}_2$  units and single atom Mo. In this paper the mass spectra of two newly synthesized quadruply bonded molybdenum complexes, whose crystals were not obtainable, are reported along with a comparison of the mass spectra of their parent compounds.

### Experimental

The mixed ligand molybdenum complexes,  $\text{Mo}_2(\text{O}_2\text{CCF}_3)_2(\text{S}_2\text{PF}_2)_2$  and  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{S}_2\text{PF}_2)_2$  by the stoichiometric reaction of  $\text{HPS}_2\text{F}_2$  as appears in literature [10].

The mass spectra of the complexes were obtained with a VG70E or mass spectrometer. A 70 eV ionization voltage was used for ionizing the samples. Samples were introduced into the ionization chamber via direct introductory probe.

### Results and Discussion

$\text{Mo}_2(\text{O}_2\text{CCF}_3)_2(\text{S}_2\text{PF}_2)_2$ . The EI mass spectrum of this compound shows the molecular ion at  $m/e$  684 which is the base peak in the fact that the cluster of peaks at 684 is due to the composition  $\text{Mo}_2(\text{O}_2\text{CCF}_3)_2(\text{S}_2\text{PF}_2)_2$  is confirmed by theoretically calculating the molecular ion peak pattern (the number and intensity of peaks). The experimental spectrum for the molecular ion in excellent agreement with that of the calculated spectrum.

Like the parent compound  $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ , from which the compound under study was prepared, loss of a fluorine atom occurs to give a fragment of  $m/e$  665. Loss of a  $\text{CF}_2\text{CO}_2$  group from the molecular ion gives an ion at  $m/e$  590; this ion was also observed in the mass spectrum [11] of  $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ . Loss of  $\text{CF}_3$  or  $\text{PF}_2$  ( $m/e$  69) from the molecular ion gives only a low-abundance ion at  $m/e$  615. The ion observed at  $m/e$  437 probably represents in part the loss of  $\text{PF}_2\text{S}_2$  and  $\text{PFS}_2$  fragments. This ion also appears in the spectrum of  $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ , but with lower relative intensity than that observed for mixed ligand compounds. The peak at  $m/e$  195, assignable to  $\text{MoOC}_2\text{F}_3^+$ , is also observed here like that of the parent compound. A series of low mass ions at  $m/e$  162, 146 and 130 are observed all of which show isotopic cluster characteristic of one molybdenum. They may be assigned to  $\text{MoS}^+$  (or

TABLE I. *m/e* VALUES AND INTENSITY OF PEAKS FOR THE MOLECULAR ION OF  $\text{Mo}_2(\text{O}_2\text{CCF}_3)_2(\text{S}_2\text{PF}_2)_2$ .

<i>m/e</i>	% Intensity
676	13.79
677	0.62
678	19.76
679	30.45
680	41.06
681	43.48
682	88.90
683	55.35
684	100.00
685	81.18
686	87.12
687	65.08
688	72.98
689	24.54
690	41.53

$\text{MoO}_2^+$ ,  $\text{MoOS}^+$  (or  $\text{MoO}_3^+$ ) and  $\text{MoS}_2^+$  (or  $\text{MoO}_2\text{S}^+$ ). Thus like the parent compound, this mixed ligand compound shows fragments resulting from the reapture of the metal-metal bond.

$\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{S}_2\text{PF}_2)_2$ . This compound gives its molecular ion at *m/e* 576 as the base peak. The cluster of isotopic peaks is that expected for the  $\text{Mo}_2$  unit. Fragment ions are quite weak relative to the molecular ion. The peak at *m/e* 502 results from the loss of methyl and acetate groups; extremely weak peaks (less than 5% relative intensity) at *m/e* 561 and 517 correspond to loss of a methyl group and of an acetate ligand from  $\text{M}^+$ , a process that is also observed [11] for the fragmentation of  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ , which does not lose a methyl group during fragmentation. The peak at *m/e* 443 presumably results from the loss of  $\text{PF}_2\text{S}_2$  ligand. Loss of  $\text{PF}_2$  (*m/e* 69) is not

observed as a major process unlike the fragmentation of  $\text{Mo}_2(\text{S}_2\text{PF}_2)_4$ .  $\text{Mo}_2\text{S}_3^+$  is observed at *m/e* 288. Fragments containing one molybdenum atom appears at *m/e* 130 ( $\text{MoS}^+$ ), 146 ( $\text{MoOS}^+$ ) and 162 ( $\text{MoS}_2^+$ ) resulting from the cleavage of the metal-metal bond. Large abundance of fragments containing  $\text{Mo}_2$  units above *m/e* 290 indicates the metal-metal bond is quite stable and the increased number of  $\text{PS}_2\text{F}_2$  ligands impart some instability as  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  does not show any fragment containing one Mo atom but this mixed ligand compound does.

**Acknowledgement.** The author gratefully acknowledges Dr. G. Goodlow of the Department of Chemistry, Auburn University, Auburn, Alabama, USA, for the mass spectra.

#### References

1. T.A. Stephenson, E. Bannister and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).
2. F.A. Cotton and J.G. Norman Jr., *J. Am. Chem. Soc.*, **94**, 5697 (1972).
3. T.R. Webb, C-C Cheng, E. Heavlin and R.A. Little, *Inorg. Chim. Acta*, **49**, 107 (1981).
4. J.H. Burk, G.G. Whitewell, J.T. Lembey and J.M. Burlitch, *Inorg. Chem.*, **22**, 1306 (1983).
5. J. Telsner and R.S. Drago, *Inorg. Chem.*, **23**, 1798 (1984).
6. J.V. Brencic and F.A. Cotton, *Inorg. Chem.*, **8**, 7 (1969).
7. J.L. Templeton, *Progr. Inorg. Chem.*, **26**, 216 (1980).
8. W.K. Bratton, F.A. Cotton, M. Debeau and R.A. Walton, *J. Coord. Chem.*, **1**, 121 (1971).
9. F.A. Cotton, A.H. Reid, Jr. and W. Schwotzer, *Inorg. Chem.*, **24**, 3965 (1985).
10. M.Q. Islam, W.E. Hill and T.R. Webb, *J. Fluorine Chem.*, **48**, 429 (1990).
11. F.A. Cotton and J.G. Norman, Jr., *J. Coord. Chem.*, **1**, 161 (1972).
12. E. Hochberg, P. Walks and E.H. Abott, *Inorg. Chem.*, **13**, 1824 (1974).