Mass spectroscopic evidence for the formation of mixed-metal octahedral clusters $[Mo_nW_{6-n}Cl_{14}]^{2-}$

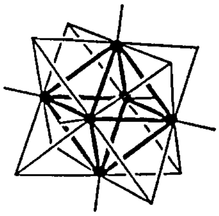
Hamdallah A. Hodali, Hoying Hung and Duward F. Shriver
Department of Chemistry, Northwestern University, Evanston, IL 60208 (USA)

Abstract

Mixed-metal clusters containing molybdenum and tungsten have been prepared by reducing $MoCl_5$ and WCl_6 with aluminum in a NaCl–$AlCl_3$ melt. Liquid secondary ion mass spectra of the product indicates the presence of seven-metal clusters across the full range, $n=0$ to 6 for $[Mo_nW_{6-n}Cl_{14}]^{2-}$. The distribution of molybdenum and tungsten in the clusters is dependent on the Mo/W ratio in the starting melt, and is biased in favor of molybdenum.

Introduction

Mixed-metal organometallic clusters of the middle and late d-block elements are well known and systematic routes to their preparation have been developed [1]. Aside from dinuclear systems, mixed-metal clusters are rare for the early d-block elements. Recently a Mo–W tetranuclear mixed-metal cluster, $Mo_2W_2Cl_8(PR_3)_4$, was reported [2]. The objective in the present work was to prepare mixed-metal clusters related to the well-known compounds $[M_6Cl_{14}]^{2-}$ (M = Mo or W) which consist of an octahedral metal framework with face-bridging and terminal halide ligands, A [3, 4]. These metal–metal bonded clusters exhibit interesting electrochemical and photochemical properties [5–10]. Liquid secondary ion mass spectrometry (LSIMS), which has been used to identify large molecules and metal clusters [11–16], was employed in the present research to identify mixed-metal clusters.



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Experimental

All manipulations of starting materials were performed in a purified nitrogen atmosphere in a dry box. Cluster syntheses were carried out in an evacuated vitreous silica tube. Tungsten(VI) chloride and molybdenum(V) chloride (Aldrich) were mixed with anhydrous aluminum chloride (Aldrich) which had been purified by sublimation at 220 °C from 1% NaCl and 1% Al powder. $[H_3O]_2[Mo_6Cl_{14}]\cdot 6H_2O$ and $[H_3O]_2$-$[W_6Cl_{14}]\cdot 6H_2O$ were prepared by literature procedures [6, 7].

The synthesis of the mixed-metal clusters was patterned after procedures for the pure molybdenum and tungsten clusters [6, 7]. In a typical synthesis an intimate mixture of equimolar quantities of $MoCl_5$ (3.42 g, 12.5 mmol), WCl_6 (4.97 g, 12.5 mmol), Al (0.35 g, 13 mmol), $AlCl_3$ (6.67 g, 50.0 mmol) and NaCl (4.3 g, 74.0 mmol) were sealed in an evacuated fused-silica tube and the mixture was heated at 200 °C for 6 h. The temperature was then raised to 450 °C over a period of 3 h and held at that temperature for 9 h. Finally, the temperature was raised to 550 °C and the reaction tube was left at that temperature for 24 h. The tube was allowed to cool to room temperature, opened in an inert atmosphere and the contents were dissolved in 1 M HCl (200 ml). The resulting solution was filtered and the residue was extracted with ethanol (50 ml). Both the filtrate and ethanol were combined and reduced in volume until the solid began to separate. Concentrated HCl was added to precipitate the cluster and NaCl. The resulting yellow solid was filtered, dried and extracted with dry ethanol. The ethanolic solution was reduced in volume, concentrated HCl was added, and the product was obtained as bright yellow needles upon slow evaporation. This procedure also was followed with a 5:1 molar ratio of $MoCl_5$:WCl_6.

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Calibration of the relative mass spectrometric intensities of the Mo_6 cluster relative to the W_6 cluster was performed on an intimate 1:1 mixture of $[Mo_6Cl_{14}]^{2-}$ and $[W_6Cl_{14}]^{2-}$, which was prepared by dissolving equimolar quantities of $[H_3O]_2]Mo_6Cl_{14}]\cdot 6H_2O$ (0.1218 g, 0.1000 mmol) and $[H_3O]_2[W_6Cl_{14}]\cdot 6H_2O$ (0.1745 g, 0.1000 mmol) in ethanol. The solvent was removed from this clear yellow solution under reduced pressure to give a yellow powder.

Mass spectra were obtained on a VG-70SE double-focusing high-resolution mass spectrometer equipped with a VG 11/250J data system. The samples were dissolved in ethanol, and *m*-nitrobenzyl alcohol (m-NBA) was used as matrix for LSIMS. Cesium iodide was used as the primary Cs^+ ion source. The primary ion beam (1 μA at 30 kV) impinged on the liquid sample surface. Negative ion detection was used for all spectra. A resolution of 2000 was employed.

The reliability factor for each envelope corresponding to isotopomers of a particular cluster was calculated using

$$R = \frac{\sum K |I_c - I_m|}{\sum K |I_m|}$$

where I_c is the calculated intensity for a particular isotopomer, I_m is its measured intensity and K is a scaling factor

$$K = \frac{\sum |I_m|}{\sum |I_c|}$$

TABLE 1. Reliability factor (R) between the simulated and observed isotopic ion distributions

Peak no.	Assignment	R[a]
1	$[Mo_6Cl_{13}]^-$	6.37[b]
2	$[Mo_6Cl_{14}]^-$	8.30[b]
3	$[Mo_5WCl_{13}]^-$	4.33
4	$[Mo_5WCl_{14}]^-$	10.77
5	$[Mo_4W_2Cl_{13}]^-$	12.27
6	$[Mo_4W_2Cl_{14}]^-$	11.54
7	$[Mo_3W_3Cl_{13}]^-$	9.00
8	$[Mo_3W_3Cl_{14}]^-$	15.38
9	$[Mo_2W_4Cl_{13}]^-$	13.52
10	$[Mo_2W_4Cl_{14}]^-$	13.06
11	$[MoW_5Cl_{13}]^-$	11.50
12	$[MoW_5Cl_{14}]^-$	13.59
13	$[W_6Cl_{13}]^-$	9.41[b]
14	$[W_6Cl_{14}]^-$	14.97[b]

[a] 20 data points were used to calculate R for each envelope with the exception of envelopes with low intensities where the outer features approached the background noise 11(17), 13(9), 14(18).
[b] R values for these clusters in the calibration mixture are: 1(1.81), 2(3.42), 13(2.91), 14(1.68).

The number of isotopomers (data points) included in this calculation for each envelope is indicated in Table 1.

Electrochemical measurements were performed with a BAS 100A electrochemical analyzer using CH_2Cl_2 as solvent, 0.1 M $[Bu_4][PF_6]$ as electrolyte, *c.* 10^{-3} M cluster, a Pt working electrode, and Ag/AgCl reference electrode. Ferrocene was used as a calibrant.

Results and discussion

The negative ion LSIMS spectrum of a homogeneous mixture of the standard consisting of equimolar quantities of $[Mo_6Cl_{14}]^{2-}$ and $[W_6Cl_{14}]^{2-}$ is shown in Fig. 1. The spectra of both molybdenum and tungsten clusters are characterized by the appearance of two envelopes representing the cluster anions $[M_6Cl_{14}]^-$ and $[M_6Cl_{13}]^-$. Weak envelopes corresponding to $[M_6Cl_{12}]^-$ and $[M_6Cl_{11}]^-$ are observed in the case of the tungsten cluster only. The two clusters also differ in the relative intensities of $[M_6Cl_{14}]^-$ relative to $[M_6Cl_{13}]^-$. For the tungsten cluster, the envelope representing the anion $[W_6Cl_{14}]^-$ has the higher relative intensity, but in the case of molybdenum $[Mo_6Cl_{13}]^-$ is more intense. The assignment for each envelope was confirmed by the reliability factors between the calculated and observed isotopic distributions for each anion shown in Fig. 1 and listed in Table 1.

The negative-ion LSIMS spectrum of the product obtained from the reaction of equimolar quantities of $MoCl_5$ and WCl_6 is shown in Fig. 2. At the extremes of this spectrum two prominent adjacent envelopes are observed; one pair for the molybdenum cluster and the other for the tungsten cluster. In agreement with the standard, these represent cluster anions $[M_6Cl_{14}]^-$ and $[M_6Cl_{13}]^-$, with peaks pairs 1, 2 and 13, 14 corresponding to the homonuclear metal clusters $[Mo_6Cl_{13}]^-$, $[Mo_6Cl_{14}]^-$ and $[W_6Cl_{13}]^-$, and $[W_6Cl_{14}]^-$, respectively.

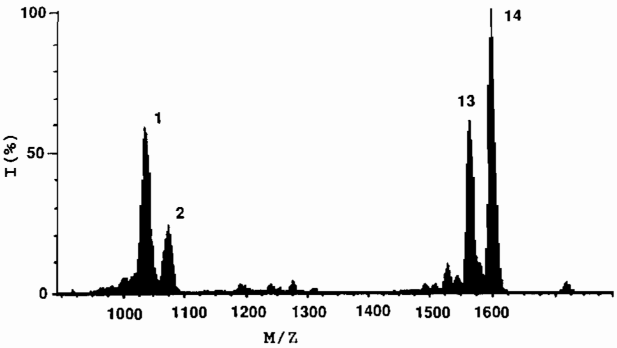

Fig. 1. Positive ion liquid secondary ion mass spectrum of an equimolar mixture of $[Mo_6Cl_{14}]^{2-}$ (1 and 2) and $[W_6Cl_{14}]^{2-}$ (13 and 14).

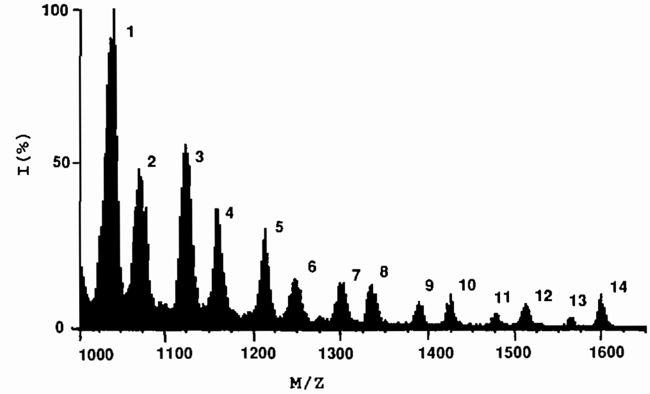

Fig. 2. Positive ion liquid secondary ion mass spectrum of the mixed-metal clusters $[W_nMo_{6-n}Cl_{14}]^{2-}$; $n=0$–6. Peaks 1 and 2 for $n=0$; 3 and 4 for $n=1$ ...etc.

In the middle of the mass spectrum the peak pairs represent the mixed Mo/W clusters. For examples, peaks 3 and 4 represent the mixed-metal clusters $[WMo_5Cl_{13}]^-$ and $[WMo_5Cl_{14}]^-$, respectively, and so on. These assignments were confirmed by the calculated and observed isotopic distributions shown in Table 1. The *R* values indicate a close match between the simulated and observed patterns. The relatively higher *R* values for the intermediate clusters (5–13) are probably due to the interference from fragments which are evident in the mass range 1175–1325 for the W_6 cluster, Fig. 1. Another notable feature of the spectrum, is the gradual decrease in the intensities of the peaks with increasing proportion of tungsten in the clusters. The relative abundance of the different clusters was estimated using the LSIMS spectrum for the standard (Fig. 1). Using a linear extrapolation of the calibration between the Mo and W standards the following relative abundances were estimated: $[Mo_6Cl_{14}]^{2-}$, 100; $[Mo_5WCl_{14}]^{2-}$, 61.3; $[Mo_4W_2Cl_{14}]^{2-}$, 34.0; $[Mo_3W_3Cl_{14}]^{2-}$, 16.0; $[Mo_2W_4Cl_{14}]^{2-}$, 8.7; $[MoW_5Cl_{14}]^{2-}$, 4.6; $[W_6Cl_{14}]^{2-}$, 3.4.

The mass spectrometric abundance of clusters having different Mo/W ratios was dependent on the Mo to W ratio in the starting melt. For example, the LSIMS spectrum of a starting melt with a molar ratio of 5:1, $MoCl_5$ to WCl_6 shows all seven clusters with higher intensity for the molybdenum-containing clusters relative to the material prepared from a 1:1 ratio of $MoCl_5$ to WCl_6. The high proportion of molybdenum in these clusters is in qualitative agreement with the more robust nature of $[Mo_6Cl_{14}]^{2-}$ in comparison with $[W_6Cl_{14}]^{2-}$, but it is contrary to the relative metal–metal bond energies in molybdenum and tungsten metal. Although the terminal members of the series have characteristic redox properties, the $[Mo_nW_{6-n}Cl_{14}]^{2-}$ material was electroactive over a very broad range with no resolution of the specific components.

Conclusions

The present clusters, $[Mo_nW_{6-n}Cl_{14}]^{2-}$ ($n=0$ to 6), and a similar series for the mixed Group 5 metals $[Nb_nTa_{6-n}Br_{14}]$ [17] are not readily separated into the individual cluster components. The separation of both of these series is apparently complicated by the very similar structures and properties within the Group 5 mixed clusters and within the Group 6 clusters. Meyer and McClarley [18] have demonstrated that the reduction of $TaCl_5$–$MoCl_5$ mixtures with aluminum in molten $AlCl_3$–NaCl, followed by work-up yields $[Ta_4Mo_2Cl_{18}]^{2-}$ and $[Ta_5MoCl_{18}]^{3-}$. The difference in charge in the Group 5/Group 6 mixed metal systems facilitates separation of these mixed metal systems. The present research shows that it is possible to demonstrate the existence and approximate concentrations in the much more homogeneous series $[Mo_nW_{6-n}Cl_{14}]^{2-}$, where there is little prospect of chemical separation.

Acknowledgements

This research was supported by the US Department of Energy Basic Energy Sciences Program, Grant DE-FG02-86ER13640. We appreciate the aid of Rachel Espe. H. Hodali was a Fulbright Fellow for the duration of this research.

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