Inorganica Chimica Acta, 198–200 (1992) 623–626

Procedures for the conversion of $\mu_2S \rightarrow \mu_2O$ in trinuclear $Mo(IV)_3$ incomplete cuboidal Mo/S cluster complexes

Qiu-Tian Liu, Jiaxi Lu* and A. Geoffrey Sykes**

Department of Chemistry, The University, Newcastle upon Tyne NE1 7RU (UK)

Abstract

The reaction of trinuclear $Mo(IV)_3$ incomplete cuboidal complexes $[Mo_3S_4(H_2O)_9]^{4+}$, $[Mo_3OS_3(H_2O)_9]^{4+}$ and $[Mo_3O_2S_2(H_2O)_9]^{4+}$ with BH_4^- in aqueous HCl solutions results in the conversion of core ligands μ_2-S to μ_2-O. In combination with Dowex cation-exchange chromatography the procedure can be used on a preparative scale. Treatment of $[Mo_3O_3S(H_2O)_9]^{4+}$ with BH_4^- results in loss of the trinuclear structure rather than μ_3-S → μ_3-O replacement. The reaction of BH_4^- with $[Mo_4S_4(H_2O)_{12}]^{5+}$ gives quantitative reduction to $[Mo_4S_4(H_2O)_{12}]^{4+}$. From these studies it is possible to better understand preparative procedures for conversion of di-μ-sulfido $Mo(V)_2$ to cuboidal Mo_4S_4 and trinuclear $Mo(IV)_3$ incomplete cuboidal $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$ complexes. Similar reactivity of the W analogue $[W_3S_4(H_2O)_9]^{4+}$ with BH_4^- is observed.

Introduction

Over the last six years cuboidal $[Mo_4S_4(H_2O)_{12}]^{n+}$, $n=4$, 5 and 6, and trinuclear incomplete cuboidal $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$ complexes have aroused considerable interest [1–3]. X-ray crystal structure determinations, particularly those by the Cotton and Shibahara groups, have provided invaluable information in the process of characterising such complexes [2, 3]. A review of relevant structures has recently appeared [4]. Mechanistic studies relating to the preparation and reactivity of the clusters have been carried out [1, 5–7]. In this paper we are concerned with the interconversion of core sulfido to oxo ligands, and a better understanding of the reactivities of such ligands. The preparative route which is most widely used involves BH_4^- reduction of di-μ-sulfido $Mo(V)_2$, which has a four-membered Mo_2S_2 ring. The $Mo(III)_4$ cube $[Mo_4S_4(H_2O)_{12}]^{4+}$, generated by the facial overlap of two such BH_4^- reduced rings, is air-oxidised to give $[Mo_4S_4(H_2O)_{12}]^{5+}$. Further air oxidation of $[Mo_4S_4(H_2O)_{12}]^{5+}$ in 2 M HCl yields $[Mo_3S_4(H_2O)_9]^{4+}$, a reaction which is essentially quantitative on heating to ~90 °C for 3–4 h. It has been suggested that by a process of edge rather than face overlap of Mo_2S_2 rings the trinuclear $Mo(IV)_3$ complex $[Mo_3OS_3(H_2O)_9]^{4+}$ is obtained as a primary product [1]. The $[Mo_3O_2S_2(H_2O)_9]^{4+}$ and $[Mo_3O_3S(H_2O)_9]^{4+}$ trinuclear complexes are best obtained (~70% yields) by an alternative route involving heating $[MoCl_6]^{3-}$ with the di-μ-sulfido and μ-oxo-μ-sulfido $Mo(V)_2$ complexes, respectively [1]. However Shibahara *et al.* have obtained the latter two trinuclear complexes from the BH_4^- procedure in amounts sufficient for X-ray crystal structure characterisation [8, 9]. We explore further these findings and seek to provide a mechanistic understanding of such processes.

Experimental

Complexes

Stock solutions of the trinuclear $Mo(IV)_3$ incomplete cuboidal complexes $[Mo_3S_4(H_2O)_9]^{4+}$, $[Mo_3OS_3(H_2O)_9]^{4+}$, $[Mo_3O_2S_2(H_2O)_9]^{4+}$ and $[Mo_3O_3S(H_2O)_9]^{4+}$, concentrations 4–12 mM in 2.0 M HCl, were prepared as described in ref. 1. Solutions (~1.2 mM) in 2.0 M $HClO_4$ were also obtained. The procedures involve purification by Dowex 50W-X2 cation-exchange chromatography to known UV–Vis spectra [1]. Samples of $[Mo_4S_4(H_2O)_{12}]^{5+}$ [1] and $[W_3S_4(H_2O)_9]^{4+}$ [10, 11] were also prepared.

Other reagents

Reducing agents sodium borohydride, $NaBH_4$, (Aldrich), and sodium dithionite, $Na_2S_2O_4$ (Fluka), were used as supplied.

Procedure

Excess of BH_4^- in H_2O (50 ml) was added to the trinuclear complex (50–100 ml), to give final concen-

---

*Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China.

**Author to whom correspondence should be addressed.

0020-1693/92/$5.00

trations of complex ~1 mM. Reaction with different amounts of BH_4^- giving 50–300-fold excesses were explored. On addition of BH_4^- dissolved in H_2O there was a rapid change in colour from green to dark green or brown according to the concentration of H^+ used. Solutions of trinuclear complexes (1–2 mM) in $HClO_4$ did not permit a sufficiently wide variation of $[H^+]$ to be carried out. Checks at the higher $HClO_4$ values gave similar results to those in HCl, although amounts of the various products were not quantified. In the case of $[Mo_3O_3S(H_2O)_9]^{4+}$ it was necessary to use HCl because the possible product $[Mo_3O_4(H_2O)_9]^{4+}$ is known to be unstable in $HClO_4$ over periods < 1 day [12]. No ionic strength adjustments were made. The solutions were allowed to stand for 30 min at room temperature.

To determine the products solutions at the higher $[H^+]$ values were diluted to 0.1 M and loaded on a Dowex 50W-X2 cation-exchange column (1.6×20 cm). The products were separated on the column using HCl, and then eluted with 1–2 M $HClO_4$. All reactions were carried out air-free, but ion-exchange columns were not rigorously air-free except with $[Mo_4S_4(H_2O)_{12}]^{5+}$ as reactant. The order of elution of $Mo(IV)_3$ complexes was $[Mo_3O_3S(H_2O)_9]^{4+}$ (red), $[Mo_3O_2S_2(H_2O)_9]^{4+}$ (grey), $[Mo_3OS_3(H_2O)_9]^{4+}$ (green) and $[Mo_3S_4(H_2O)_9]^{4+}$ (green). Some 50 ml of 1 M $HClO_4$ was required to elute separately the first two complexes, followed by ~50 ml of 2 M $HClO_4$ to the other two complexes. The identity and amounts of product were determined by UV–Vis spectrophotometry: $[Mo_3S_4(H_2O)_9]^{4+}$ (peak at 602 nm, $\epsilon = 351\ M^{-1}\ cm^{-1}$ per trinuclear); $[Mo_3OS_3(H_2O)_9]^{4+}$ (588, 263); $[Mo_3O_2S_2(H_2O)_9]^{4+}$ (572, 202); $[Mo_3O_3S(H_2O)_9]^{4+}$ (512, 153); $[Mo_4S_4(H_2O)_{12}]^{5+}$ (645, 435 per cube); and $[Mo_7S_8(H_2O)_{12}]^{8+}$ (635, 1266 per double cube) [1, 13]. Percentage yields of product were based on the amount of Mo recovered. Total recoveries were < 100% due to the formation of some precipitate, particularly at the lower $[H^+]$ values (this collected at the top of Dowex columns), and the formation of unidentified Mo products. The smell of H_2S was detected during the 30 min of reaction.

Results

Reaction of $Mo_3S_4(H_2O)_9]^{4+}$

Results from three experiments are shown in Table 1. Recoveries were 76% at $[H^+] = 0.02$ M, and 90% at the two higher $[H^+]$ values. Features are the replacement of μ_2-S by μ_2-O to give $[Mo_3OS_3(H_2O)_9]^{4+}$ and $[Mo_3O_2S_2(H_2O)_9]^{4+}$ products. At the two lower $[H^+]$ values there is also a tendency to form the double cube $[Mo_7S_8(H_2O)_{18}]^{8+}$ [14]. The latter is known to give the single cube which may be the source of the latter product [6]. When dithionite was used as reductant (30:1 excess) at $[H^+] = 0.20$ M, a precipitate was obtained, and no coloured cationic products were isolated on the Dowex column. With a 4.5:1 ratio of reductant to complex 59% of the $[Mo_3S_4(H_2O)_9]^{4+}$ was retained, and 31% of $[Mo_3OS_3(H_2O)_9]^{4+}$ was formed.

TABLE 1. Product analyses for the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ (1.2 mM) with BH_4^- (0.5 M) in HCl. Dowex separation after 30 min reaction time at ~20 °C

$[H^+]$ (M)	$Mo_3S_4^{4+}$ (%)	$Mo_3S_3O^{4+}$ (%)	$Mo_3S_2O_2^{4+}$ (%)	$Mo_4S_4^{5+}$ (%)	$Mo_7S_8^{8+}$ (5)
0.02	32	15	2	14	14
0.20	35	36	9	10	1
1.00	45	41			

TABLE 2. Product analyses for the reaction of $[Mo_3OS_3(H_2O)_9]^{4+}$ (1.0 mM) with BH_4^- (0.5 M) in HCl. Dowex separation after 30 min reaction time at ~20 °C

$[H^+]$ (M)	$Mo_3OS_3^{4+}$ (%)	$Mo_3O_2S_2^{4+}$ (%)	$Mo_3O_3S^{4+}$ (%)
0.05	51	49	
0.20	56	27	7

TABLE 3. Product analyses for the reaction of $[Mo_3O_2S_2(H_2O)_9]^{4+}$ (1.5 mM) with BH_4^- (0.5 M) in HCl. Dowex separation after 30 min reaction time at ~20 °C

$[H^+]$ (M)	$Mo_3O_2S_2^{4+}$ (%)	$Mo_3O_3S^{4+}$ (%)
0.025	45	17
0.20	51	12

Reaction of $[Mo_3OS_3(H_2O)_9]^{4+}$

For the two $[H^+]$ values studied 99% and 90% recoveries were observed, Table 2. Again the μ_2-S → μ_2-O replacement was noted. No double cube formation was observed.

Reaction of $[Mo_3O_2S_2(H_2O)_9]^{4+}$

Recoveries were considerably reduced (~60%) for the two $[H^+]$ values investigated, Table 3. A possible explanation of this loss becomes apparent on considering the results for $[Mo_3O_3S(H_2O)_9]^{4+}$ below.

Reaction of $[Mo_3O_3S(H_2O)_9]^{4+}$

The acid used was HCl so that any $[Mo_3O_4(H_2O)_9]^{4+}$ formed could be retained. Substantial loss of trinuclear complex was indicated. The product analysis, Table 4, indicates no $[Mo_3O_4(H_2O)_9]^{4+}$ formation. Therefore the μ_3-S → μ_3-O conversion does not readily take place.

TABLE 4. Product analyses for the reaction of $[Mo_3O_3S(H_2O)_9]^{4+}$ (1.5 mM) with BH_4^- in HCl. Dowex separation after 30 min reaction time at ~20 °C. No trinuclear or other complexes detected

Excess BH_4^-	H^+ (M)	$Mo_3O_3S^{4+}$ (%)
230	0.3	0
106	0.4	37
106	0.2	25
51	0.2	68

Other experiments

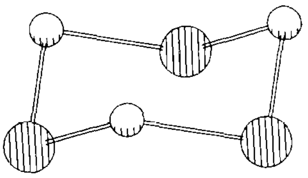
With a 300:1 excess of BH_4^- over $[Mo_4S_4(H_2O)_{12}]^{5+}$, $[H^+]=0.25$ M, there was quantitative conversion to air-sensitive $[Mo_4S_4(H_2O)_{12}]^{4+}$. Two experiments with 0.1 mM $[W_3S_4(H_2O)_9]^{4+}$, $[BH_4^-]$ in 400-fold excess, $[H^+]=0.10$ M and 0.20 M, gave ~45% retention of $W_3S_4^{4+}$, with ~23% of $W_3OS_3^{4+}$ as product.

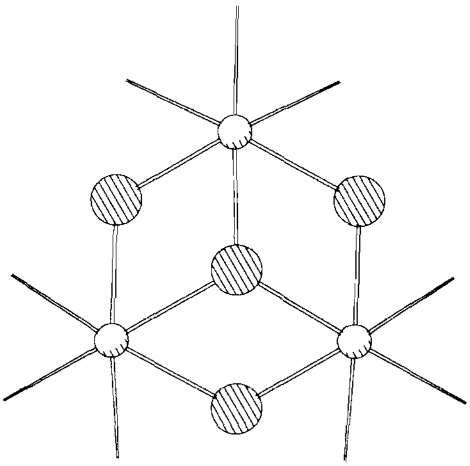
Discussion

A number of observations are possible from the experiments carried out. First and foremost is the relative ease of replacement of μ_2-S by μ_2-O, which can be achieved with retention of the $Mo(IV)_3$ trinuclear structure. Thus $[Mo_3S_4(H_2O)_9]^{4+}$ is converted to $[Mo_3OS_3(H_2O)_9]^{4+}$ and $[Mo_3O_2S_2(H_2O)_9]^{4+}$ in amounts which can be used on a preparative scale. With $[Mo_3S_4(H_2O)_9]^{4+}$, and in only this case, the reducing action of the BH_4^- brings about $Mo(IV)_3$ to cube formation. This may occur via $[Mo_7S_8(H_2O)_{18}]^{8+}$ in a reaction previously reported [6]. The two cube forms generated, $[Mo_4S_4(H_2O)_9]^{5+}$ and $[Mo_7S_8(H_2O)_{18}]^{8+}$, have lower (average) oxidation states (<3.5) than the trinuclear $Mo(IV)_3$ complexes. Although $[Mo_4S_4(H_2O)_{12}]^{5+}$ and not $[Mo_4S_4(H_2O)_{12}]^{4+}$ is the final product, $[Mo_4S_4(H_2O)_{12}]^{4+}$ is most likely present in the early stages when BH_4^- is still present. In all experiments excess BH_4^- rapidly decays by reaction with H^+ to give H_2.

In separate experiments quantitative BH_4^- reduction of $[Mo_4S_4(H_2O)_{12}]^{5+}$ to $[Mo_4S_4(H_2O)_{12}]^{4+}$ was observed. The cubes have all μ_3-S ligands, and no reaction of μ_3-S is observed. In the case of $[Mo_3O_3S(H_2O)_9]^{4+}$ there is likewise no replacement of μ_3-S by μ_3-O. The outcome in the latter is somewhat different since the trinuclear structure is not retained. A similar trend is also observed with $[Mo_3O_2S_2(H_2O)_9]^{4+}$, when less Mo is recovered in the form of 4+ trinuclear products.

Since S^{2-} bridging ligands cannot be further reduced the prime process involving BH_4^- must be reduction of Mo(IV) to Mo(III) followed by a labilisation and replacement of μ_2-S by μ_2-O with involvement of H_2O solvent. A feature of $Mo_3S_4^{4+}$ is the non-planar Mo_3S_3 ring structure, the six Mo to μ_2-S bonds which have an average length of 2.281 ± 0.017, intermediate between the single Mo–S bond length of 2.44 Å, and the double Mo=S bond length of 2.08 Å. A theory of quasi-aromaticity has been proposed by Lu, in which the bonding in the Mo_3S_3 ring is compared to that of benzene [15]. The conformation of the Mo_3S_3 ring is retained in the presence of the μ_3-S apical ligand as illustrated. For the mixed oxo-sulfido containing $Mo_3O_xS_{3-x}$ rings, similar arguments presumably apply.





A single rate determining Mo to μ_2-S bond cleavage may be sufficient to initiate the replacement process. To achieve a μ_3-S to μ_3-O replacement more extensive bond breaking is required. Notably in the case of the $[Mo_3O_3S(H_2O)_9]^{4+}$ complex loss of structure results, and the trinuclear Mo_3O_3S core is no longer retained.

In other experiments it has been demonstrated that $S_2O_4^{2-}$ is a more effective reductant than BH_4^-. At high concentrations (30:1 excess) the trinuclear $[Mo_3S_4(H_2O)_9]^{4+}$ structure is destroyed. At 4.5:1 concentrations it provides an effective means of bringing about $\mu_2\text{-S} \rightarrow \mu_2\text{-O}$ conversion.

Finally the same sort of $\mu_2\text{-S} \rightarrow \mu_2\text{-O}$ conversion is observed with $[W_3S_4(H_2O)_9]^{4+}$ although $W(IV)_3$ is more difficult to reduce than $Mo(IV)_3$.

Acknowledgement

We are grateful to the Chinese Academy of Science for a Fellowship (to Q.-T.L).

References

1 M. Martinez, B.- L. Ooi and A. G. Sykes, *J. Am. Chem. Soc., 109* (1987) 4615.

2 F. A. Cotton, Z. Dori, R. Llusar and W. J. Schwotzer, *J. Am. Chem. Soc., 107* (1985) 6734.

3 T. Shibahara, H. Kuroya, K. Matsumoto and S. Ooi, *Inorg. Chim. Acta, 116* (1987) L25.

4 T. Shibahara, *Adv. Inorg. Chem., 37* (1990) 143–173.

5 B.-L. Ooi, C. Sharp and A. G. Sykes, *J. Am. Chem. Soc., 111* (1989) 125.

6 B.-L. Ooi and A. G. Sykes, *Inorg. Chem., 28* (1989) 3799.

7 Y.-J. Li, M. Nasreldin, M. Humanes and A. G. Sykes, *Inorg. Chem.,* in press.

8 T. Shibahara, T. Yamada, H. Kuroya, E. F. Hills, P. Kathirgamanathan and A. G. Sykes, *Inorg. Chim. Acta, 113* (1986) L19.

9 T. Shibahara, H. Hattori and H. Kuroya, *J. Am. Chem. Soc., 106* (1984) 2710.

10 T. Shibahara, K. Kohda, A. Ohtsuji, K. Yasuda and H. Kuroya, *J. Am. Chem. Soc., 108* (1986) 2757.

11 M. Nasreldin, A. Olatunji, P. W. Dimmock and A. G. Sykes, *J. Chem. Soc., Dalton. Trans.,* (1990) 1765.

12 B.-L. Ooi and A. G. Sykes, *Inorg. Chem., 27* (1988) 310; P. Kathirgamanathan, A. B. Soares, D. T. Richens and A. G. Sykes, *Inorg. Chem., 24* (1985) 2950.

13 D. T. Richens and A. G. Sykes, *Inorg. Chem., 21* (1982) 418.

14 T. Shibahara, T. Yamamoto, H. Kanadani and H. Kuroya, *J. Am. Chem. Soc., 109* (1987) 2950.

15 J.-X. Lu, *Jiegou Huaxue, 8* (1989) 337.