

## Substitution on Five $\mu$ -Oxo/ $\mu$ -Sulphido Incomplete Cuboidal $\text{Mo}^{\text{IV}}_3$ Ions $[\text{Mo}_3\text{O}_x\text{S}_{4-x}(\text{H}_2\text{O})_9]^{4+}$ : Kinetic Effects Resulting from the Replacement of Core Oxo by Sulphido Ligands

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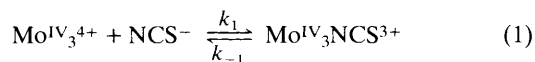
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A 570-fold spread in rate constants (25 °C),  $[\text{H}^+] = 2.0 \text{ M}$ , is observed for 1 : 1  $\text{NCS}^-$  substitution (of  $\text{H}_2\text{O}$ ) at Mo on the title complexes, with replacement of core  $\mu_3(\text{O})$  by  $\mu_3(\text{S})$  decreasing (factor of 10), and further replacement of the three  $\mu_2(\text{O})$  by  $\mu_2(\text{S})$  increasing (factor of 570) the rate of substitution.

The preparation<sup>1</sup> and determination of structures by X-ray crystallography<sup>2-8</sup> of five incomplete cuboidal trimeric  $\text{Mo}^{\text{IV}}$  aqua-ions in the series  $[\text{Mo}_3\text{O}_x\text{S}_{4-x}(\text{H}_2\text{O})_9]^{4+}$  ( $x = 0-4$ ) as in Table 1, have been described. There are three terminal  $\text{H}_2\text{O}$  ligands attached to each Mo. Here we focus on trends in reactivity, and the effect which replacement of core  $\text{O}^{2-}$  by  $\text{S}^{2-}$  has on the substitution of  $\text{H}_2\text{O}$  ligands.

Different Mo identities (designated e-h) arise, depending on whether the Mo is bound to three  $\mu$ -oxo-ligands as in  $[\text{Mo}_3\mu_3(\text{O})\mu_2(\text{O})_3(\text{H}_2\text{O})_9]^{4+}$  (molybdenum atoms designated e), or to different combinations of core atoms  $\mu_3(\text{S})\mu_2(\text{O})_2$  (f),  $\mu_3(\text{S})\mu_2(\text{O})\mu_2(\text{S})$  (g), or  $\mu_3(\text{S})\mu_2(\text{S})_2$  (h) as illustrated. In the case of  $[\text{Mo}_3\mu_3(\text{O})\mu_2(\text{O})_3(\text{H}_2\text{O})_9]^{4+}$ , it has been established that the  $\text{H}_2\text{O}$  ligands attached to each Mo behave differently depending on whether they are *trans* to the core  $\mu_2$ -oxo or  $\mu_3$ -oxo ligands.<sup>9</sup> Different substitution properties are observed, with the  $\text{H}_2\text{O}$  *trans* to  $\mu_2$ -oxo ligands the more labile. For  $[\text{Mo}_3\mu_3(\text{O})\mu_2(\text{O})_3(\text{H}_2\text{O})_9]^{4+}$  a statistical factor of three is relevant (because of the trimeric nature of the reactant),<sup>10,11</sup> and rate constants determined with the in-coming ligand ( $\text{NCS}^-$  or  $\text{C}_2\text{O}_4\text{H}^-$ ) in excess ( $\geq 10$ -fold) are a factor of three smaller than those with the trimer in large excess.

Forward and back rate constants ( $k_1$  and  $k_{-1}$ , 25 °C) for  $\text{NCS}^-$  studies (equation 1) are used to illustrate trends in reactivity (Table 1). Rate constants were obtained by conventional spectrophotometry (first three entries) and High-Tech SFA-11 rapid-mix or Dionex stopped-flow spectrophotometry. In all cases, rate constants with  $\text{NCS}^-$  in excess have been modified to allow for statistical factors, and are for reaction at one Mo centre.



There is a 570-fold difference in  $k_1$  values from the most inert,  $[\text{Mo}_3\mu_3(\text{S})\mu_2(\text{O})_3(\text{H}_2\text{O})_9]^{4+}$ , to the most labile,  $[\text{Mo}_3\mu_3(\text{S})\mu_2(\text{S})_3(\text{H}_2\text{O})_9]^{4+}$ , of these ions. Closer examination of the data reveals a 10-fold decrease in  $k_1$  on replacing  $\mu_3(\text{O})$  in  $[\text{Mo}_3\mu_3(\text{O})\mu_2(\text{O})_3(\text{H}_2\text{O})_9]^{4+}$  by  $\mu_3(\text{S})$  to give  $[\text{Mo}_3\mu_3(\text{S})$

$\mu_2(\text{O})_3(\text{H}_2\text{O})_9]^{4+}$ . However, on replacing the  $\mu_2(\text{O})$ 's by  $\mu_2(\text{S})$  quite the opposite effect is observed, giving a substantial increase in lability of the  $\text{H}_2\text{O}$ 's.

In the case of  $[\text{Mo}_3\mu_3(\text{S})\mu_2(\text{O})\mu_2(\text{S})_2(\text{H}_2\text{O})_9]^{4+}$  biphasic kinetics are observed,<sup>12</sup> and rate constants for two concurrent processes are obtained. One of these (the slower), requiring a statistical factor of two to obtain a correspondence of rate constants with first  $\text{NCS}^-$  and then  $\text{Mo}^{\text{IV}}$  in ten-fold excess, is identified as substitution at the Mo's of type g, and the other is therefore for substitution at the Mo of type h. Similarly  $[\text{Mo}_3\mu_3(\text{S})\mu_2(\text{O})_2\mu_2(\text{S})(\text{H}_2\text{O})_9]^{4+}$  provides another example of non-equivalent  $\text{Mo}^{\text{IV}}$  sites. Only one rate constant has so far been determined, and since a statistical factor of two is required, this process is assigned to substitution at the  $\text{Mo}^{\text{IV}}$ 's of type g. The  $\text{H}_2\text{O}$ 's co-ordinated to the third  $\text{Mo}^{\text{IV}}$ , which is bonded to two  $\mu_2(\text{O})$ 's are expected to substitute more slowly.

An additional feature is the unexpectedly high acid dissociation for  $\text{H}_2\text{O}$  ligands of  $[\text{Mo}_3\mu_3(\text{O})\mu_2(\text{O})_3(\text{H}_2\text{O})_9]^{4+}$ ,  $K_a = 0.42 \text{ M}$  from the kinetics in toluene-*p*-sulphonic acid (HPTS),  $I = 2.0 \text{ M}$  (LiPTS), where it has been demonstrated that

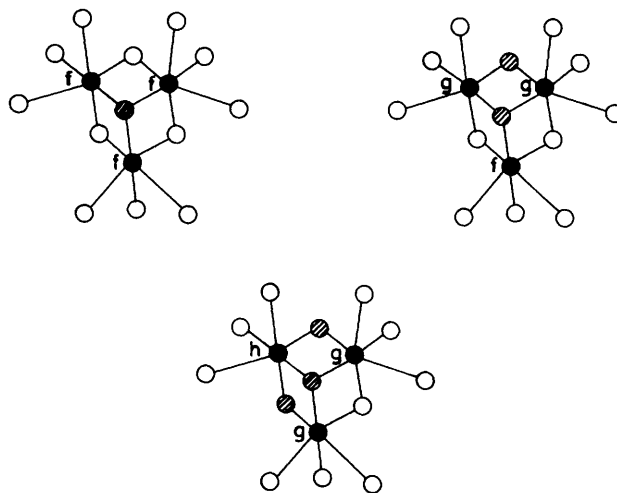
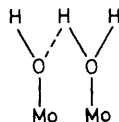


Table 1. Summary of rate constants (25 °C) for equilibration with  $\text{NCS}^-$  in 2.0 M- $\text{HClO}_4$ ,  $I = 2.0 \text{ M}$ .

Complex	Type of Mo	$k_1$ ( $\text{M}^{-1}\text{s}^{-1}$ )	$k_{-1}$ ( $\text{s}^{-1}$ )	$K_1$ ( $\text{M}^{-1}$ )
$[\text{Mo}_3\mu_3(\text{O})\mu_2(\text{O})_3(\text{H}_2\text{O})_9]^{4+}$ <sup>a</sup>	e	2.13	$2.2 \times 10^{-3}$	968
$[\text{Mo}_3\mu_3(\text{S})\mu_2(\text{O})_3(\text{H}_2\text{O})_9]^{4+}$	f	0.37	$1.6 \times 10^{-4}$	2310
$[\text{Mo}_3\mu_3(\text{S})\mu_2(\text{O})_2\mu_2(\text{S})(\text{H}_2\text{O})_9]^{4+}$	f	not determined <sup>b</sup>		
	g	7.7	$2.7 \times 10^{-3}$	2850
$[\text{Mo}_3\mu_3(\text{S})\mu_2(\text{O})\mu_2(\text{S})_2(\text{H}_2\text{O})_9]^{4+}$	g	23	$1.4 \times 10^{-3}$	1640
	h	82	$2.4 \times 10^{-2}$	3420
$[\text{Mo}_3\mu_3(\text{S})\mu_2(\text{S})_3(\text{H}_2\text{O})_9]^{4+}$	h	212	$9.2 \times 10^{-2}$	2300

<sup>a</sup> Data from ref. 10. <sup>b</sup> Absorbance changes are small.



substitution proceeds solely by the conjugate-base form.<sup>11</sup> The behaviour of  $[\text{Mo}_3\mu_3(\text{S})\mu_2(\text{O})_3(\text{H}_2\text{O})_9]^{4+}$  is similar. The high acid dissociation may stem from proton bridging, as has been detected for other transition-metal complexes.<sup>13,14</sup> From the X-ray crystal structures on complexes with the  $\text{Mo}_3\text{O}_4^{4+}$  core, it is clear that for the aqua-ion adjacent Mo's have approximately parallel Mo-OH<sub>2</sub> bonds, Mo-Mo separation 2.52 Å,<sup>3</sup> which is appropriate for such bonding. However with  $[\text{Mo}_3\mu_3(\text{S})\mu_2(\text{S})_3(\text{H}_2\text{O})_9]^{4+}$ , which has an Mo-Mo separation of 2.77 Å,<sup>8</sup> the conjugate-base pathway has also been identified and  $K_a$  is of similar magnitude, a finding which is currently being further explored.

These various effects, in particular the opposing trends which we report on replacing  $\mu_3(\text{O})$  by  $\mu_3(\text{S})$  (less labile H<sub>2</sub>O's) and  $\mu_2(\text{O})$  by  $\mu_2(\text{S})$  (more labile H<sub>2</sub>O's), clearly have implications with regard to the bonding of O<sup>2-</sup> as compared to S<sup>2-</sup> in these clusters. Such trends attributable to  $\sigma$ - and  $\pi$ -bonding effects have been discussed extensively in the context of Pt<sup>II</sup> square-planar substitution reactions<sup>15</sup>, but are more difficult to appraise for octahedral and, in this instance, cluster-type complexes. A further effect is that which geometric distortions stemming from the replacement of O<sup>2-</sup> by the bigger S<sup>2-</sup> might have (note the different rate constants for **g** and **h** Mo's in Table 1). From our most recent preparative work,<sup>1</sup> an apical  $\mu_3$ -oxo ligand does not appear to be compatible with  $\mu_2$ -sulphido ligands, and the existence of such complexes has not been confirmed in our recent studies.

On replacing oxo by sulphido ligands equilibrium constants  $K_1$  (Table 1) exhibit no systematic trend and the four-fold variation is mild compared with the kinetic effect on  $k_1$ . We note that for studies in 2 M-HClO<sub>4</sub>  $k_1$  is a composite term incorporating  $K_a$ . Values of  $K_a$  are of similar magnitude for  $[\text{Mo}_3\mu_3(\text{O})\mu_2(\text{O})_3(\text{H}_2\text{O})_9]^{4+}$  and  $[\text{Mo}_3\mu_3(\text{S})\mu_2(\text{S})_3(\text{H}_2\text{O})_9]^{4+}$ , and we have no reason to suppose that the pattern of rate constants in Table 1 will change much on taking this factor into account.

B.-L. O. thanks the University of Newcastle upon Tyne for a Ridley Fellowship, and M. M. the University of Barcelona for leave, and the British Council for support.

Received, 15th February 1988; Com. 8/00536B

## References

- 1 M. Martinez, B.-L. Ooi, and A. G. Sykes, *J. Am. Chem. Soc.*, 1987, **109**, 4615.
- 2 A. Bino, F. A. Cotton, and Z. Dori, *J. Am. Chem. Soc.*, 1978, **100**, 5252; 1979, **101**, 3842; *Inorg. Chim. Acta*, 1979, **33**, L133.
- 3 E. O. Schlemper, M. S. Hussain, and R. K. Murmann, *Cryst. Struct. Commun.*, 1982, **11**, 89.
- 4 S. F. Gheller, T. W. Hambley, R. T. C. Brownlee, M. J. O'Connor, M. R. Snow, and A. R. Wedd, *J. Am. Chem. Soc.*, 1983, **105**, 1627.
- 5 T. Shibahara, H. Hattori, and H. Kuroya, *J. Am. Chem. Soc.*, 1984, **106**, 2710.
- 6 T. Shibahara, T. Yamada, H. Kuroya, E. F. Hills, P. Kathirgamanathan, and A. G. Sykes, *Inorg. Chim. Acta*, 1986, **113**, L19.
- 7 T. Shibahara, H. Miyake, K. Kobayashi, and H. Kuroya, *Chem. Lett.*, 1986, 139.
- 8 F. A. Cotton, Z. Dori, R. Llusar and W. Schwotzer, *J. Am. Chem. Soc.*, 1985, **107**, 6734; *Inorg. Chem.*, 1986, **25**, 3654; T. Shibahara and H. Kuroya, *Polyhedron*, 1986, **5**, 357; A. Müller, R. Jostes, W. Eltzner, C.-S. Nie, E. Diemann, H. Bogge, M. Zimmerman, M. Dartman, U. Reinsch-Vogell, Che Shun, S. J. Cyvin, and B. N. Cyvin, *Inorg. Chem.*, 1985, **24**, 2872.
- 9 K. R. Rodgers, R. K. Murmann, E. O. Schlemper, and M. E. Shelton, *Inorg. Chem.*, 1985, **24**, 1313; G. D. Hinch, D. E. Wycott, and R. K. Murmann, *Polyhedron*, 1986, **5**, 487; D. T. Richens, L. Helm, P.-A. Pittet, and A. E. Merbach, *Inorg. Chim. Acta*, 1987, **132**, 85, and personal communication.
- 10 P. Kathirgamanathan, A. B. Soares, D. T. Richens, and A. G. Sykes, *Inorg. Chem.*, 1985, **24**, 2950.
- 11 B.-L. Ooi and A. G. Sykes, *Inorg. Chem.*, 1988, **27**, 310.
- 12 A. A. Frost and R. G. Pearson in 'Kinetics and Mechanism,' 2nd Edn., Wiley, New York, 1961, p. 160.
- 13 M. Ardon and A. Bino, *Inorg. Chem.*, 1988, **27**, 1343.
- 14 F. Galsbol, S. Larson, B. Rasmussen, and J. Springborg, *Inorg. Chem.*, 1986, **25**, 290.
- 15 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 5th Edn., Wiley Interscience, New York, 1988, p. 1300.